A Treatise on
PHYSICAL CHEMISTRY

A Co-operative Effort by a Group of Physical Chemists

Third Edition — In Five Volumes

EDITED BY

HUGH S. TAYLOR
David B. Jones Professor of Chemistry, Princeton University

AND

SAMUEL GLASSTONE
Formerly Professor of Chemistry, The University of Oklahoma

VOLUME ONE
ATOMISTICS AND THERMODYNAMICS

THIRD PRINTING

NEW YORK

"It is also true that man sees more of the things themselves when he sees more of their origin; for their origin is a part of them and indeed the most important part of them. Thus they become more extraordinary by being explained. He has more wonder at them but less fear of them; for a thing is really wonderful when it is significant and not when it is insignificant."

G. K Chesterton—"St. Francis of Assisi."

PREFACE

Progress in the science of physical chemistry has been phenomenal in the two decades that have passed since the project for a Treatise on Physical Chemistry by the cooperative efforts of a group of physical chemists was first formulated. In the exploration of the atomic constitution of matter a great mass of detail has been added to the structure as then known. Isotopes, which were then but recently recognized, have now been found in nearly all of the chemical elements, their relative abundances accurately determined and an increasing number separated one from another. With the aid of alpha-particles and laboratory-produced projectiles the transmutation of the elements has been achieved. In addition to the naturally occurring radioactive elements there are more than three hundred and fifty other radioactive species produced by nuclear transformations. Neutrons and positrons have taken their places beside the proton and electron among the units of atomic architecture. The quantum theory of energy as developed in the first two decades of the century has been supplemented by the wave theory of matter. Electrons as well as X-rays now serve to elucidate molecular structure and indeed define molecular size and shape. Classical thermodynamics as the basis for the treatment of chemical equilibrium has been amplified by the introduction of statistical methods ever broadening in range and scope and permitting even the computation of equilibria inaccessible to experimental test. Applications of these same statistical methods to chemical kinetics have produced also a revolution in this branch of science. The theory of the liquid state and the structure of liquids now merit discussion comparable with that hitherto reserved for the solid and gaseous states. New techniques for study of surfaces and macromolecules, paralleling the brilliant advances of the synthetic organic chemist, are providing the bases for an attack on the problems of complex biochemical systems.

If, then, twenty years ago, the need for cooperative effort in the record of our science was necessary, how much the more is it imperative today. Over the years in question the standards of texts in the science have shown a steady advance so that, today, there are single-volume texts which go well beyond the scope of the cooperative effort of 1924. To set forth adequately all the great advances in the science, to define the present status of the subject, and to present to the student the accumulated experience of his predecessors in the work so that he may go forward to the new fields as yet unexplored, cannot be achieved as hitherto within the scope of two volumes. The publishers of the Treatise courageously decided to venture upon a much more ambitious enterprise, to embark on an expansion to five volumes. The cooperative feature of the effort was to be maintained. The subject was to

v

be presented in a sequence of volumes. The first was to contain an exposition of the fundamentals of Atomistics and of Thermodynamics. It was to be followed at intervals of several months by four volumes which should present in succession, the States of Matter, Chemical Equilibrium, Chemical Kinetics and finally all those diverse elements which could be grouped under the title of Molecular Structure. The scope of the work was to be so broad that the student in a special field could garner from its pages that which was known as he set forth in his quest for the unknown. With the publication of this first volume the Treatise on Physical Chemistry begins the third phase of its career the success of which, we hope, may parallel that of the preceding phases and justify the loyal assistance of the cooperating scientists.

With the growth of the effort has come increased editorial responsibility, the solution for which has again been sought by cooperation. The former editor has been indeed fortunate that he could enlist, for this third edition, the mature, experienced and competent assistance of Dr. Samuel Glasstone who, by sharing the burdens of the editorial work without stint, has made possible a more rapid transition from conception to realization. Once again, the cooperation of the publishers in the production of volumes of high technical publishing excellence will be manifest in the pages that follow. In the difficult years ahead the record of what physical chemists have already achieved should spur others to maintain and extend the place of our science in the hierarchy of knowledge.

HUGH S. TAYLOR

PRINCETON, N. J.
December,1941

CONTENTS

vii

CHAPTER I

THE ATOMIC CONCEPT OF MATTER

BY HUGH S. TAYLOR

David B. Jones Professor of Chemistry, Princeton University, N. J.

The inception of the modern era in chemical science may be attributed to the proposal of the atomic theory of chemical action by John Dalton in the first volume of his New System of Chemical Philosophy, 1808. The scientific era in which the Daltonian concept was formulated was especially favorable to its development. The theory of atomic constitution was no new theory. The Greek theory of atoms, due to Leucippus and handed down to us in the writings of Democritus, is the first of which we have record. Boyle included in his conception of elementary substances some notions of atomic constituents. Dalton himself was led to the atomic theory by reason of his admiration of the Newtonian doctrine of the atomic constitution of matter. The quantitative era into which Dalton's theory was born provided the circumstances necessary and favorable to its growth. The theory simplified and correlated much that the quantitative spirit had disclosed and had not yet explained. It provided the framework upon which was built the chemical philosophy and the chemical research of the nineteenth century Towards the close of the century it seemed as though the theory might give way to an interpretation of the science based upon energetics. But, in the new century, it emerged once more, broadened and amplified by the discoveries of sub-atomic phenomena.

(1) **The Atomic Theory**: The atomic theory of Dalton postulated the existence of minute indivisible particles or atoms, each of equal weight for the same element, atoms of different elements, however, having different weights. Compounds were the result of union of dissimilar atoms the ratio of whose weights was proportional to their combining weights. This fundamental idea of atoms having characteristic weights and combining to form chemical compounds at once illuminated the quantitative facts of chemical combination then known. They may be thus briefly summarized:

(1) *The Law of Definite Proportions*, established experimentally by Proust in 1799. The elements which form a chemical compound are united in it in an invariable ratio by weight, which is characteristic of that compound. Proust's analyses were made with carbonate of copper, artificial and natural, the two oxides of tin and the two sulfides of iron. Proust showed, in contradiction of claims put forward by Berthollet on behalf of variable composition due to mass action, that when a metal combines with oxygen in more than one proportion there is no gradual increment of one element but a sudden, *per saltum*, increment. His analytical work was not sufficiently accurate to establish the law of multiple proportions.

(2) *The Law of Multiple Proportions*, deduced from experimental work by Dalton and

1

formulated by him in conformity with his preconceived atomic theory.   When an element combines with another to form more than one compound the masses of the second element combining with a fixed mass of the first element bear a simple ratio to one another.   The accurate analyses of Berzelius provided abundant evidence of the truth of this law which the less accurate efforts of Dalton produced.

(3) *The Law of Reciprocal Proportions*, established by the experimental work of Richter (1792–1794).   When two or more elements combine with a third in certain proportions they combine with each other in the same proportions or in multiples of these proportions.   In his book *Stoichiometry of the Chemical Elements* published in the above years this law of reciprocal proportions is illustrated.

The Law of Conservation of Mass, formulated by Lavoisier in 1774 upon the basis of experimental measurement, states that the total mass of the reactants in a chemical reaction is equal to the total mass of the products of reaction.   All these laws, quantitatively exact and experimentally verifiable, fitted admirably into the framework of chemical principles established by Dalton's Atomic Theory.   Further support was quickly forthcoming.   Gay Lussac put forward in 1808 his *Law of Combining Volumes*.   When gases combine they do so in simple ratios by volumes, the volume of the gaseous product bearing a simple ratio to the volumes of the reactants when measured under the same conditions of temperature and pressure.   An attempt by Berzelius to interpret this law in terms of the atomic theory failed owing to a lack of understanding of the differences between atoms and molecules.   Knowing, as a result of the earlier investigations of Gay Lussac, that many gases vary similarly when subjected to temperature, and, from the investigations of Boyle, to pressure changes, Berzelius suggested that equal volumes of different gases under like conditions of temperature and pressure contain the same number of atoms.

(2) **Avogadro's Hypothesis:** The correct correlation of the atomic theory with the characteristics of ideal gases is due to Avogadro who propounded in 1811 the Avogadro hypothesis.   Though not accepted by the early proponents of the atomic theory and only commanding general adherence after the exposition of the hypothesis some 47 years later by his fellow countryman the Italian scientist Cannizzaro, the hypothesis of Avogadro was a true exposition of the facts concerning gases.   The hypothesis may be stated in the following terms: Equal volumes of different gases under the same conditions of temperature and pressure contain the same number of molecules.   The limitations of this hypothesis as regards actual gases and the many experimental methods which have now been developed actually to determine the number of molecules in a given volume of gas will be dealt with in appropriate portions of the following chapters.   At this stage it will suffice to indicate the actual change introduced by the Avogadro hypothesis into the Daltonian concept of atoms and atomic combinations.   On the Avogadro principle, the atom became the smallest particle which can enter into chemical combination.   The molecule became the smallest particle of matter which was capable of independent existence.   This distinction clarified the known experimental facts.   It explained, for example, how one molecule of hydrogen and one molecule of chlorine combined to form two molecules of hydrogen chloride.   Each molecule of hydrogen and chlorine

contained two atoms whereas the molecules of hydrogen chloride contained an atom each of hydrogen and chlorine. It is perhaps advisable to point out, now that the difficulties associated with the terms atom and molecule no longer exist, that the definition of the molecule given above lacks somewhat in rigor. For, we now know that, under proper conditions, not only molecules of diatomic gases such as hydrogen, chlorine and iodine may exist in the free state but that atoms may also so exist provided the conditions of temperature and pressure be suitably chosen. Under such conditions the molecule and the atom become identical.

With the atomic theory as guide, Berzelius proceeded to the determination of atomic weights of a wide variety of elementary substances. The determination involves two steps, (1) the measurement of the combining weight and (2) the finding of the ratio of combining weight to atomic weight. The former is an experimental operation generally involving some kind of quantitative analytical procedure as, for example, the determination of the quantities of potassium and chlorine in unit quantity of potassium chloride, of hydrogen and oxygen in water or of hydrogen and chlorine in hydrogen chloride. From such determinations the combining weights of oxygen, chlorine and potassium in terms of hydrogen as unity may be determined. The second step, however, involves a knowledge of the number of atoms which are combined in a compound with the reference element. Thus, to take an example of historic interest, the atomic weight of oxygen relative to that of hydrogen as unity would be approximately 8 or 16 according as one or two hydrogen atoms combine with one atom of oxygen, the combining weight being 8. It is in the solution of this problem that the Avogadro hypothesis performed a most useful function, delayed, however, by the non-recognition of the importance of the hypothesis until Cannizzaro's demonstration of its utility in such connection. Until that demonstration was given, no general agreement as to atomic weights was possible, different observers using different values which, however, were simple multiples of other values for the same element, according to the preconceived idea of the experimenter as to the atomic ratios prevailing in the compound analyzed.

(3) **Dulong and Petit's Law:** Two further principles of great utility in deciding doubtful cases of atomic weight values were discovered and employed in the early years of the atomic theory. The one, the law of Dulong and Petit was applicable to solid elementary substances. The law, formulated in 1819, states that the product of the atomic weight and the specific heat is approximately 6 calories. It will be shown that this law is a limiting law applicable to all solid elements under specified conditions Known exceptions, such as boron and carbon, which show low atomic heats at ordinary temperatures, manifest at those temperatures a phenomenon common to all solid elements if the temperature chosen for the determination be sufficiently low. At higher temperatures, even these elements have atomic heats approximating those demanded by the law. Nevertheless, a sufficiently large number of elements obey the Dulong and Petit relation at ordinary temperatures as to make this

principle of important assistance in deciding cases of doubt in reference to atomic weights deduced by other methods.

(4) **Isomorphism:** The second principle was of assistance in the study of the atomic weights of elements present in crystalline compounds. In 1820 Mitscherlich called attention to the practical identity of crystalline forms of the corresponding salts of phosphoric and arsenic acids. They crystallized with the same molecular quantities of water of crystallization and possessed the power of forming mixed crystals. As a result of such observations, Mitscherlich concluded that analogous elements or groups of elements can replace one another in compounds without material alteration of crystalline form. Two compounds so related were termed isomorphous and the phenomenon was given the name Isomorphism. The identity of form is not absolute. The distance between atoms varies slightly in one compound from that in the compound of the next analogue. These differences persist even in the mixed crystal and result in distortion of the crystal angles. The variation of interatomic distances and the distortion of the crystal angles become greater the more widely divergent are the analogous elements. As a consequence, with the more widely divergent analogues, mixed crystals will not occur even though there is identity of crystal form between the compounds. Substances may crystallize in two or more distinct crystallographic systems having, nevertheless, constant chemical composition. Such behavior is termed dimorphism. If isomorphism occurs between the two forms severally of two such dimorphous bodies the bodies are said to be isodimorphous, the phenomenon being, correspondingly, isodimorphism. Similarly, trimorphous substances are known.

From the standpoint of the atomic theory, however, quite apart from the importance of Mitscherlich's observations crystallographically, isomorphism assisted greatly, since it gave a ready indication of chemical composition in the case of substances crystallizing in the same form and isomorphously with substances of known composition. Berzelius made great use of the principle in fixing atomic weights and in checking the results of his analytical investigations. Isomorphism has acquired a still greater range of applicability as the result of more recent deductions concerning the sub-atomic characteristics of the atom. As will be later demonstrated, isomorphism is possible between compounds containing elements which from the Mitscherlich standpoint would not be regarded as analogues but which, from a similarity of sub-atomic components, acquire identity of crystalline form. (See Vol. II.)

(5) **Prout's Hypothesis:** Philosophically considered, the Daltonian concept of atoms, of differing weights but incapable of subdivision, is not without difficulties. Reason suggests the possibility of subdivision even though technique may not be adequate to its achievement. As a consequence, side by side with the many achievements of theoretical chemistry in the 19th century, based fundamentally upon the atomic theory, there has persisted the essentially opposite viewpoint, namely that of continuity or unity of matter as opposed to the discontinuous view of material substances which the atomic theory postulates. This contrary viewpoint has been developed both consciously

and unconsciously. Prout's hypothesis put forward in 1815 is the earliest illustration of conscious development. Prout, reasoning from the approximation to whole numbers of the atomic weights of several of the elements, suggested that the elements might be, in reality, polymers of hydrogen. This was a revival of the protyle theory of matter with quantitative investigations as its support. But further quantitative study tended to withdraw support from the hypothesis of Prout. The hypothesis gave an added stimulus to exact atomic weight determinations and these but served to demonstrate effectively that many of the atomic weights were markedly divergent from whole numbers. Stas's determinations of atomic weights, and notably that of chlorine, were classical researches, with this divergence from the whole number rule as the decisive result.

(6) **Döbereiner's Triads:** Attempts at classification of the elements on the basis of similarity of properties are less conscious methods of establishing the essential unity of matter. Thus, Döbereiner's observation, in 1817, that groups of three elements chemically similar, with atomic weights in arithmetic progression, could be compiled, while essentially an attempt at convenient classification, involves, in its fundamentals, an appreciation of a unifying principle. The chemical similarity of, for example, lithium, sodium and potassium, chlorine, bromine and iodine, calcium, strontium and barium, sulfur, selenium and tellurium with the very definite arithmetical relationships of their atomic weights, $Na - Li = 16.06$, $K - Na = 16.1$, suggests immediately a fundamental factor common to each group of three and so some unity underlying each group. This aspect of the matter was not, however, emphasized either in Döbereiner's triad system nor in subsequent, more comprehensive, systems of classification.

(7) **Faraday's Laws of Electrolysis:** The electrochemical researches of Nicholson and Carlisle, 1800, on the decomposition of water, of Davy on the preparation of potassium, sodium, and other metals, 1807–1808, and of Berzelius and Hisinger in Sweden, 1803–1807, on the decomposition of neutral salts by the electric current, definitely brought electrochemistry to the fore as an auxiliary to other methods of chemical investigation. Davy's electrochemical theory of affinity and Berzelius's theory of atomic polarization brought electrochemistry into the domain of theoretical chemistry. Faraday's researches in experimental electricity established quantitatively the relationship between electricity and the atomic weights of the elements. Faraday observed that (Experimental Researches, 505): 'For a constant quantity of electricity, whatever the decomposing conductor may be, whether water, saline solutions, acids, fused bodies or the like, the amount of electrochemical action is also a constant quantity.' Furthermore, with different solutions, the amounts of elementary constituents produced by unit quantity of electricity are proportional to their chemical equivalents. In these two laws the atoms and electricity are for the first time intimately associated. Faraday's ions, transferred through solutions by the agency of the current, were carried in definite amounts, one gram ion for every 96,500 coulombs of electricity. Modified by Grove, 1845, by Williamson

in 1851, and by Clausius, 1857, in the sense that the decomposition was not effected by the current but that the ion carriers must exist in part uncombined, the theory of conduction was given quantitative formulation by Arrhenius, 1887, who then assumed that the extent to which the free ions occurred in solution was deducible from the electrical conductance of the solution as well as from the properties of solutions, at that time entirely disassociated from the electrical properties of solutions, namely, osmotic phenomena, freezing point, boiling point and vapor pressures of solutions. The properties of conducting solutions became a function of the positively and negatively charged ions which they contained. Progress from this point of view to those held today came as a result of the researches of the physicist and the student of radioactive change.

(8) **The Periodic System of Classification:** Before the contributions of the physics of the atom and of radioactivity were achieved, the chemist had provided himself with a broad and comprehensive system of classification of the elements which, more decisively than hitherto, suggested a fundamental unity of elementary structure, though designed, primarily, to emphasize the interrelation of chemical and physical properties. An effort of de Chancourtois (Vis Tellurique, Classement naturel des Corps Simples, 1862) excited little attention among chemists, though substantially a statement of periodicity of properties with increase of atomic weight. Newland's Law of Octaves, 1864, an arrangement of the elements in groups of eight bringing with each eighth element a repetition of properties like the eighth note of an octave in music, aroused much ridicule and little respect, though essentially the correct formulation of periodicity. It is noteworthy to record that, had Ramsay's discovery of the rare gases of the atmosphere preceded this formulation, the analogy with the musical octave would have been lost; the scoffers would have lacked one of their principal weapons of ridicule. Mendeleeff in 1869 established the same periodicity of properties by arranging the elements in the order of increasing atomic weights. His historic association with the law arises because he employed the periodic law, so discovered, as a powerful instrument of chemical classification and a weapon for prosecuting chemical research.

"When I arranged the elements," he wrote, "according to the magnitude of their atomic weights, beginning with the smallest, it became evident that there exists a kind of periodicity in their properties. I designate by the name periodic law the mutual relations between the properties of the elements and their atomic weights; these relations are applicable to all the elements and have the nature of a periodic function."

Simultaneously, Lothar Meyer in Germany was evolving the same generalization. Meyer was more concerned with the periodic variation in the *physical* properties of the elements as a periodic function of the atomic weights of the elements, his graph of atomic volume plotted against atomic weight demonstrating the same broad periodic relationship which we may now detail as the result of the application of the Mendeleeff principle.

The accompanying table embodies the ideas as laid down by Mendeleeff with the modifications introduced by newer and better data than were available to Mendeleeff and modified also by the additions—especially that of

Group 0, which comprises the rare gases of the atmosphere—which subsequent research and discovery have permitted. For convenience in subsequent discussion, the table has been amplified by the insertion of the atomic numbers of the elements as well as the atomic weights. The table is in its essentials, however, identical with that of Mendeleeff. It contains 9 vertical columns or groups and 12 horizontal rows termed series or periods. Hydrogen is in a series by itself. It possesses the properties of the elements of Group I in certain of its compounds, that of Group VII in others.[1] Following hydrogen come two *short periods* of eight elements each, falling naturally into the eight groups from Group 0 to Group VII, helium to fluorine in the first of these two series, neon to chlorine in the second. Beyond chlorine, the next thirty-six elements fall naturally on the basis of properties into two groups of eighteen, the two first *long periods*, argon to bromine in the first, krypton to iodine in the second. These groups of eighteen show a variation from the two short periods in that three elements in each period, so called transitional elements, iron, cobalt, nickel and ruthenium, rhodium and palladium are grouped together in Group VIII. This arrangement was devised by Mendeleeff as a result of obvious difficulties in placing them in other groups and by reason of their close similarity one to another. By the arrangement indicated, krypton and xenon come into Group 0 with the other rare gases. The other members of the various groups fall naturally into the classification on the basis of similarity of properties. Mendeleeff arranged the remaining elements in three *long periods* in which there were many gaps, but in which the similarity of chemical and physical properties provided a sure guide for allocation. It is now known, as will be later discussed in detail, that, following the second period of eighteen comes a longer period of thirty-two elements of which the initial element is xenon, the last element, Number 85. This long period is succeeded by an incomplete fragment, of which the initial element is the emanation of radium, a gas of the rare gas type, and of which the heaviest known element, uranium, is the last member of the series occurring in nature. Element No. 93 is produced by transmutation processes (see later). The first long period of thirty-two elements contains a trio of similar elements, osmium, iridium and platinum, as in the groups of eighteen, these being assigned likewise to Group VIII. The rare earth elements are also members of this long period of thirty-two.

The Mendeleeff arrangement brings together, in one group, elements which have general family properties, physical and chemical, which vary gradually from first to last and which resemble one another more closely than do any of the other elements. This similarity and gradual variation suggests some common feature of internal construction or architecture. In the series, or horizontal lines of the table, there is a marked difference from member to member in physical and especially in chemical properties. Thus, for example in the matter of maximum oxide forming capacity, the variation of a series is

[1] H_2O—Na_2O; HCl—$NaCl$; $LiCl$—LiH. See: Peters, *Z. anorg. Chem.*, **131**, 140 (1923); Bardwell, *J. Am. Chem. Soc.*, **44**, 2499 (1922).

TABLE I
THE PERIODIC TABLE

Periods	Group 0	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
Formula of highest oxide	—	R_2O	RO	R_2O_3	RO_2	R_2O_5	R_2O_6	R_2O_7	RO_4
Formula of hydride	—	RH	RH_2	RH_3	RH_4	RH_3	RH_2	RH	—
First short period	He 18 4.003	H 1 1.008 · Li 3 6.940	Be 4 9.02	B 5 10.82	C 6 12.010	N 7 14.008	O 8 16.000	F 9 19.00	
Second short period	Ne 10 20.183	Na 11 22.997	Mg 12 24.32	Al 13 26.97	Si 14 28.06	P 15 30.98	S 16 32.06	Cl 17 35.457	
First long period — Even Series	A 18 39.944	K 19 39.096	Ca 20 40.08	Sc 21 45.10	Ti 22 47.90	V 23 50.95	Cr 24 52.01	Mn 25 54.93	Fe 26 55.85 Co 27 58.94 Ni 28 58.69
First long period — Odd Series	Kr 36 83.7	Cu 29 63.57	Zn 30 65.38	Ga 31 69.72	Ge 32 72.60	As 33 74.91	Se 34 78.96	Br 35 79.916	
Second long period — Even Series		Rb 37 85.43	Sr 38 87.63	Y 39 88.92	Zr 40 91.22	Cb 41 92.91	Mo 42 95.95	Ma 43	Ru 44 101.7 Rh 45 102.91 Pd 46 106.7
Second long period — Odd Series	Xe 54 131.3	Ag 47 107.880	Cd 48 112.41	In 49 114.76	Sn 50 118.70	Sb 51 121.76	Te 52 127.61	I 53 126.92	
Third long period — Even Series		Cs 55 132.91	Ba 56 137.36	La 57 138.92	Ce 58 140.13				
Third long period — Odd Series			The Rare Earth Elements Pr 59 to Yb 71						
Fourth long period — Even Series					Hf 72 178.6	Ta 73 180.88	W 74 183.92	Re 75 186.31	Os 76 190.2 Ir 77 193.1 Pt 78 195.23
Fourth long period — Odd Series		Au 79 197.2	Hg 80 200.61	Tl 81 204.39	Pb 82 207.21	Bi 83 209.00	Po 84	−85	
Fifth long period	Rn An Tn 86 222	−87	Ra 88 226.05	Ac 89	Th 90 232.12	Pa 91	U 92 238.07		

from an element with no power of combination, the rare gas, through elements with respective oxides R_2O, RO, R_2O_3, RO_2, R_2O_5, R_2O_6, R_2O_7 and in some cases R_2O_8. Each series, however, more or less resembles the series which preceded it, with one proviso. In the long periods there are two series, the so-called 'odd' and 'even' series. Examination will show that the 'even' series 4, 6 and 8 resemble one another, 5 and 7 also, much more so than do the 'even' series resemble the 'odd.' On the basis of indivisible atoms this factor receives no elucidation. It was merely observed and accepted in the original classification. The explanation must be sought and, as will be shown, is found in the architecture of the atom. As observed above with the oxides, the maximum state of oxidation progressively increases from left to right in a series. It should be observed also that the elements show a minimum valence in hydride formation, rising from 0 to 4 as we pass from a rare gas such as helium to a member of Group IV such as carbon. Beyond Group IV, however, the combining power falls as indicated by the compounds NH_3, OH_2, FH. This factor also lacked elucidation in the original formulation of the periodic law.

The Applications of the Periodic Law: As pointed out by Mendeleeff the periodic law could be employed in: (1) The classification of the elements; (2) The estimation of atomic weights; (3) The prediction of properties of unknown elements; (4) The correction of atomic weights.

(1) In the classification of the elements the periodic arrangement has never been surpassed nor superseded. It is still a most useful and convenient method of classifying the data of inorganic chemistry whether of elements or of compounds.

(2) Mendeleeff assigned to indium an atomic weight of 113.4 on the basis of Winkler's value of 37.8 for the equivalent weight; this makes indium trivalent, gives it place in Group III of the table between cadmium and tin, below gallium, where it fits very well. Specific heat measurements of indium metal confirmed the correctness of this assignment.

(3) Mendeleeff used the table to predict the properties of missing elements in Group III and Group IV akin to boron, aluminum and titanium. The predictions concerning eka-boron, eka-aluminum and eka-silicon were abundantly justified and confirmed in the subsequent discoveries of scandium, gallium and germanium respectively.

(4) Mendeleeff predicted corrections in the atomic weights of osmium, iridium and platinum which gave to them this order rather than that given by the order of atomic weights accepted in 1870 which would have given platinum, iridium, osmium. The periodic law has not, however, always been the successful guide in corrections to accepted atomic weights as will now be discussed.

The Defects of the Periodic Law: On placing elements in the order of atomic weights two outstanding anomalies presented themselves to Mendeleeff. Tellurium, being assigned an atomic weight greater than that of iodine, would have passed into the halogen group, while iodine would have been placed in the oxygen, sulfur, selenium group. This would have been an obvious inversion of the periodicity of properties. Since the atomic weight of iodine had been many times checked and rechecked, so that considerable certainty could be attached to its value, Mendeleeff suggested that the atomic weight of tellurium must be wrong, that the correct value would be between 123 and 126 instead of the then accepted value of 128. Hence ensued a vigorous study

of tellurium, its purity, purification and atomic weight determination. Efforts were made in abundance to separate therefrom some constituent of higher atomic weight which would have a position below tellurium in the 6th group. All these efforts were fruitless. A multiplicity of methods of purification all failed to yield a tellurium of atomic weight lower than that of iodine. The exception did not nullify the periodic law. The wonderful truth and value of the periodic relation were abundantly evident. As a consequence, and until the reason for the anomaly should reveal itself, tellurium and iodine were assigned to those group positions to which their properties, chemical and physical, indicated that they belonged, order of atomic weights notwithstanding.

Cobalt (58.94) and nickel (58.69) were similarly misplaced on the basis of order of atomic weights. The sequence from the standpoint of properties of the first three transitional elements is most certainly iron, cobalt, nickel, whereas the order of atomic weights is iron, nickel, cobalt. Again, the presence of another element, 'gnomium,' was suspected. Again, intensive and painstaking labors failed to reveal the element or reverse the order of atomic weights. Cobalt and nickel likewise remained anomalous.

One other pair of misfits arose with the discovery of the rare gases by Ramsay. Argon of atomic weight 39.944, an obvious member of Group 0, was found to have an atomic weight greater than that of potassium, 39.096, again obviously a member of Group I. In view of these anomalies in the face of such overwhelming evidences of the approximate truth of the law in the majority of its details it is little wonder that Ramsay asked "Why this incomplete concordance?" The answer has emerged and in the unfolding of the mystery the student of chemical philosophy has much to learn. He will find an answer to the query of Ramsay. The incomplete concordance is evidence of the limitations to which many laws are subject, is evidence that the laws in question are but *approximations* to the fundamental law. The incomplete concordance is evidence of incomplete truth. The realization of this will be valuable, for it will give to authentic exceptions to general laws a vital importance in the search for truth. Science is full of illustrations of this fact. The exceptions to the Law of Dulong and Petit were an index of the approximate truth only of the law. It will be shown later that they constituted a sign post to a more fundamental law of the specific heats of elements of which Dulong and Petit's Law is but a limiting case. Ramsay himself found in the anomalous density of nitrogen from air and from nitrogen compounds as determined by Lord Rayleigh the sign post to a whole group of chemical elements at that time unknown. The anomalies in the periodic law were the arrows pointing to the necessity of obtaining yet more fundamental truths concerning the nature, the architecture and the periodic relationships of elementary matter. As the science progressed new sign posts appeared. The allocation of the rare earths to positions in the periodic table was a problem in itself of great complexity. The discovery of the radio-elements multiplied the difficulties of allocation. These difficulties gave to other less pronounced difficulties an added significance. Thus, for example, the problem of the odd

and even series recurs. Copper, silver and gold are distinct variants from the alkali elements. Gold chloride, $AuCl_3$, seems out of place in the compounds of the elements of Group I. Lead resembles thallium, mercury is similar to copper. Magnesium behaves like manganese in some of its compounds. In the ultimate solution, such problems will find their elucidation.

(9) **The Periodic Law and Electrochemistry**: Faraday concluded that the laws of electrochemical action which he deduced were consonant with the facts of the atomic theory. Subsequent researches of Grove, Clausius, Hittorf, and Arrhenius established that, in conducting solutions, the elementary constituents were present, not as atoms, but as charged ions. It is of interest to examine the nature of these postulated ions in terms of the Mendeleeff classification. In a simple solution of an electrolyte, say of sodium chloride, the ionic theory postulated the presence of positively charged sodium ions and negatively charged chloride ions

$$NaCl + aq. = Na^+ \ (aq.) + Cl^- \ (aq.).$$
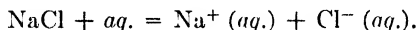
With an electrolyte such as barium chloride the solution contained barium ions with a doubly positive charge and twice the number of singly charged negative ions

$$BaCl_2 + aq. = Ba^{++} \ (aq.) + 2Cl^- \ (aq.).$$
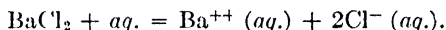
With sodium sulfide on the other hand the opposite distribution of charges was postulated

$$Na_2S + aq. = 2Na^+ \ (aq.) + S^{--} \ (aq.).$$
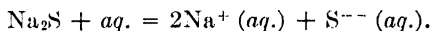
Similarly, aluminum chloride dissociates thus:

$$AlCl_3 + aq. = Al^{+++} \ (aq.) + 3Cl^- \ (aq.).$$
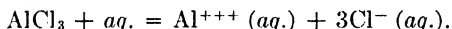
In terms of electrochemical theory, therefore, the elements of Group I yield univalent positive ions, Group II bivalent positive ions, Group III tervalent positive ions. Group VII contains the elements yielding univalent negative ions, Group VI elements yielding bivalent ions, Group V the tervalent negative ions, though these are rare. On the left of Group IV are to be found the pronouncedly electro-positive elements, to the right the more pronouncedly electronegative compounds. These facts are of importance in the ensuing development of atomic structure. They provide a background from which to approach the newer ideas.

(10) **Atomic Structure**: The atomic theory of Dalton provides, as has been shown, a satisfactory basis for the laws of chemical combination and the atomic weight provides a useful, if not completely satisfactory, basis for the classification of the elements. The concept of definite and indivisible atoms, of different weights, could not, however, be the ultimate solution of the problem of material structure. It provides no answers to a variety of problems. The difference in chemical properties between two atoms, say hydrogen and oxygen, can never be satisfyingly relegated to a simple difference in weight. Wherein does the

difference in weight lie? What factors determine the weight difference? Furthermore, a number of physical and chemical properties of elementary substances cannot be explained upon any basis of weight variation of ultimate indivisible particles. The varying valence of the different elements and also the varying valences of a single element remain entirely unexplained on the basis of the simple atomic theory. The spectral differences among the elements are likewise unexplainable. As has already been emphasized, the similarity and periodicity of properties, both physical and chemical, is the strongest possible evidence that like elements must possess similarities of architecture not envisaged by a theory of indivisible atoms. The inadequacies of the periodic system of classification are further sign posts indicating the need for further exploration of the composition of the individual atoms. Dalton had a glimpse from whence progress might come, for in his address to the Royal Society, upon receiving the Royal Medal he stated:

"The causes of chemical change are as yet unknown, and the laws by which they are governed; but, in their connexion with electrical and magnetic phenomena there is a gleam of light pointing to a new dawn in science."

(11) **The Electron:** It is of interest to note that the development of the concept of atomic structure commenced when the concept of atomic electricity received its first quantitative study. Faraday's experiments on the conduction of salt solutions are the first experiments indicative of discrete units of electricity. G. Johnstone Stoney in an address before the British Association in 1874, published in 1881,[1] definitely emphasizes this fact.

"Nature presents us with a single definite quantity of electricity which is independent of the particular bodies acted on. To make this clear, I shall express Faraday's Law in the following terms, which, as I shall show, will give it precision, viz.: For each chemical bond which is ruptured within an electrolyte a certain quantity of electricity traverses the electrolyte which is the same in all cases."

Helmholtz in the Faraday lecture at the Royal Institution in 1881 emphasized the same point of view:

"Now the most startling result of Faraday's Law is perhaps this, if we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions which behave like atoms of electricity."

G. Johnstone Stoney, 1891, gave to the 'natural unit of electricity,' thus defined in reference to Faraday's Law, the name 'electron.' Faraday's Law, however, was not sufficient to establish the atomistic concept of electricity. It applied only to solutions of electrolytes. Metallic conduction was still discussed in terms of 'ether strains' and 'continuous homogeneous fluids.' The proof of atomic electricity did not come until the mechanism of gaseous conduction had been studied and the properties of gases acted upon by X-radiation and radioactive materials had become familiar.

[1] *Phil. Mag.*, 11, 384 (1881).

The experiments of J. J. Thomson and his collaborators at the Cavendish Laboratory, Cambridge, England, supplied the original information in this field.   Gases treated with X-rays were found to be conducting.   The conductivity thus induced in a gas was caused by an agency which could be removed by filtration through glass wool, by passage of the gas through metal tubes or between plates maintained at a sufficiently large potential difference.   The conductivity was therefore due to electrically charged particles.   More detailed knowledge of the nature of the charged particles was obtained by a study of the conduction of electricity through gases at low partial pressures. When currents at high potentials are discharged through gases at pressures of about 0.01 mm. or lower, charged particles or corpuscles are shot off from the cathode.   These particles, first investigated by Sir Wm. Crookes, and called by him the 'fourth state of matter,' have properties the study of which led eventually to an appreciation of their importance in atomic structure.   The cathode particles were shown to have the following properties:

(1) They travel in straight lines normal to the cathode and cast shadows of opaque objects placed in their path.

(2) They are capable of producing mechanical motion.

(3) They produce phosphorescence in many objects exposed to their action, e.g., blue phosphorescence in lead glasses.

(4) They produce a rise in temperature in objects which they strike.

(5) They may be deflected, by electromagnetic and electrostatic fields, from their normal rectilinear paths.

(6) The charge carried by the particles is negative since they electrify negatively insulated metallic electrodes upon which they fall.

(7) They may penetrate thin sheets of metal, the stopping power of the metal varying directly with the thickness of the metal and with its density.

(8) They act as nuclei for the condensation of supersaturated vapors.   The fogs thus formed are useful as a means of rendering the particles visible.

(9) The particles were identical in nature and in the ratio of charge to mass of the particles, *irrespective of the nature of the residual gas in the discharge tube or of the metals used in the electrodes.*

(12) **The Velocity of the Cathode Particle:** The velocity of the particle can be determined by measuring the displacement effected by known electrostatic and electromagnetic fields on a fine pencil of cathode particles.   Such a pencil of particles impinging on a phosphorescent screen may be located by the phosphorescent spot produced.   If a strong magnetic field H be applied to such a pencil of rays they will be deflected from their rectilinear path.   The force exerted by the field H on a particle carrying a charge e, moving with a velocity v, will be Hev.   At equilibrium, this force will be equal to the centrifugal force of the moving particle acting outwards along its radius of curvature, r.   Therefore, if the mass of the particle be m, the following relation holds

$$\mathrm{H}ev = \frac{mv^2}{r} \cdot \qquad (12.1)$$

Since H and r are both measurable it follows that the ratio $mv/e = $ Hr can be

determined. Now, by superposing on the pencil of cathode particles thus magnetically deflected a suitable electrostatic field X, the pencil may be restored to its original rectilinear path. In such case, by equating the electrostatic and electromagnetic forces involved, there follows

$$Xe = Hcv, \qquad (12.2)$$

whence v may be determined from the known values of X and H. Hence also the ratio e/m may be obtained.

By removing the electromagnetic field, a further check upon the value of e/m may be obtained. The electrostatic field deflects the corpuscles from their normal rectilinear path. The downward acceleration (= force/mass) produced by the action of the electrostatic field is Xe/m. The distance through which the particle will fall in time t is

$$d = \frac{1}{2} \cdot \frac{Xet^2}{m}. \qquad (12.3)$$

Now $t = l/v$ where l is the distance travelled by a particle of velocity v. Hence, the vertical displacement, d, as revealed by the change in position of the phosphorescent spot is given by

$$d = \frac{1}{2} \cdot \frac{Xe}{m} \cdot \frac{l^2}{v^2}. \qquad (12.4)$$

Since d and l may be measured, X is known and v deduced as indicated above, it is possible to calculate e/m from the equation

$$\frac{e}{m} = \frac{2d}{X} \cdot \frac{v^2}{l^2}. \qquad (12.5)$$

By these methods Thomson was able to show that the ratio e/m was constant for all cathode rays, irrespective of the nature of the electrodes or the nature of the residual gas in the discharge tube for all velocities of travel not approaching the velocity of light. The average value of v was found to be 2.8×10^9 cm. per second. The value of e/m in such discharge tubes was approximately 1.79×10^7 electromagnetic units (e.m.u.). This may be compared with the ratio of e/m for a hydrogen ion. It was known that the charge carried by such an ion is about 4.8×10^{-10} electrostatic unit (e.s.u.). The mass of a hydrogen ion is 1.64×10^{-24} gram. Hence in electromagnetic units, the charge e/m for a hydrogen ion is

$$\frac{4.8 \times 10^{-10}}{1.64 \times 10^{-24} \times 3 \times 10^{10}} = 0.97 \times 10^4 \text{ electromagnetic units.}$$

For the cathode particle therefore the ratio e/m is approximately

$$\frac{1.79 \times 10^7}{0.97 \times 10^4} = 1845 \text{ times}$$

greater than that for the hydrogen ion. It is apparent that one of several factors may account for this: (1) either the charge on the particle is some 1845 times greater than that on the hydrogen ion, the masses being identical, or (2) the mass of the particle may be 1/1845 of the mass of the hydrogen ion and the charges identical or (3) the cathode particle may differ in both charge and mass from that of the hydrogen ion. It will now be shown that the charge of the cathode particle is identical with that of the hydrogen ion and that, therefore, the mass of the cathode particle is approximately 1/1845 of the hydrogen ion.

(13) **The Charge Carried by a Cathode Particle:** The earliest efforts to determine the charge, e, were made by Townsend,[1] J. J. Thomson [2] and H. A. Wilson.[3] Townsend and Thomson determined the total charge carried by a cloud formed around ions suitably produced, the total weight of the cloud and the average weight of the component water droplets by observation of their rate of fall under gravity, the mean radius being computed by application of Stokes's Law

$$v = \frac{2}{9} \cdot \frac{gr^2 d}{\eta}, \tag{13.1}$$

where v is the velocity of fall of a drop of water of radius r and density d, falling through a gas of viscosity η under the acceleration of gravity, g.

H. A. Wilson studied the rate of fall of the cloud under gravity alone and also under the combined action of gravity and an electrostatic field. The ratio of the velocities, v_1 and v_2, under gravity alone and with the combined action of gravity and an electrostatic field X is given by the equation

$$\frac{v_1}{v_2} = \frac{mg}{mg + Xe}. \tag{13.2}$$

Combining this with (13.1) for v_1, and eliminating m by the equation $m = \tfrac{4}{3}\pi r^3 d$, Wilson obtained the expression

$$e = \left\{ \tfrac{4}{3}\pi \left(\frac{9\eta}{2g} \right)^{3/2} \right\} \frac{g}{X} \cdot \frac{(v_2 - v_1)}{d^{1/2}} v_1^{1/2}. \tag{13.3}$$

This yielded for e a mean value of 3.1×10^{-10} e.s.u. The deviations were considerable, the extreme values being 2.0×10^{-10} and 4.4×10^{-10} e.s.u. Wilson's method eliminated the assumption as to the equality of the number of droplets and the number of ions. It involved the assumption, however, that successive cloud formations gave equally sized droplets, an assumption which later work by Millikan could not be found to sustain with any certainty.

Millikan's first work with Begeman was essentially a repetition of the H. A. Wilson method using radium as the ionizing agent and a 4000 volt storage battery to charge the

[1] *Proc. Camb. Phil. Soc.*, **9**, 244 (1897).
[2] *Phil. Mag.*, **46**, 528 (1898).
[3] *Ibid.*, **5**, 429 (1903).

plates.   The results were more consistent than Wilson's and gave as the mean of the observations, varying between 3.66×10^{-10} and 4.37×10^{-10}, a value $e = 4.06 \times 10^{-10}$ e.s.u.[1]

Millikan's 'Balanced-drop' Method:[2] This represents a distinct advance on the H. A. Wilson method.   To eliminate errors due to evaporation, Millikan planned to use a sufficiently strong field, to balance exactly the force of gravity on the droplets and thus maintain the top surface of the cloud stationary. Without attaining this object, he succeeded in the more important task of studying the behavior of *individual droplets*.   He found they could be held suspended in the field from 30 to 60 seconds; that they carried multiple charges varying between $2e$ and $6e$.   These charges were all exact multiples and therefore reveal positively the unitary nature of electricity.   The ionized cloud after formation between the plates was subjected to a given potential gradient. This removes all of the cloud particles with the exception of those which have the right ratio of charge to mass to be held in suspension in the field.   Observations on these droplets were made with a telescope in the eyepiece of which three equally spaced cross hairs were placed.   A small section of the space between the plates was illuminated by a narrow beam of light suitably freed from its heat rays by three water cells in series.   The cross hairs were set near the lower plate and as soon as a stationary drop was found somewhere above the upper cross hair it was watched for a few seconds to make sure that it was not moving.   The field was then thrown off and the plates shortcircuited. The drop was then timed in its fall by means of a stop-watch as it passed across the three cross hairs.   It will be seen that this method furnishes a check upon evaporation; for, if the drop is stationary at first it is not evaporating sufficiently to influence the readings; if it begins to evaporate before the readings are completed, the time required to pass through the second space should be greater than that required to pass through the first space.   In general this was not the case.

The preceding equation (13.3) of the Wilson method, applied to the balanced droplet, assumes the form

$$e = 3.422 \times 10^{-9} \frac{g}{X} (v_1)^{3/2}. \tag{13.4}$$

In this case, the electrostatic field X is so opposed to gravity that $v_2 = 0$. The constant 3.422×10^{-10} was chosen by Millikan as most accurately representing the terms in the Wilson equation involving the viscosity of the medium and the density of the droplets.   From these determinations, Millikan deduced the value $e = 4.65 \times 10^{-10}$ e.s.u., with extreme values of 4.87×10^{-10} and 4.56×10^{-10} e.s.u.

Millikan's Oil Drop Method:[3] This later method of Millikan's represents the most accurate method of determination of the unitary quantity of electric-

[1] *Phys. Rev.*, **26**, 198 (1908).
[2] *Phil. Mag.*, **19**, 209 (1910).
[3] *Phys. Rev.*, **2**, 143 (1913).

ity disclosed by the previously mentioned investigation. A diagram of this apparatus is appended. The droplets investigated were introduced into the chamber D by means of the atomizer A in the form of a finely divided spray. Eventually one of these droplets finds its way through the aperture, p, into
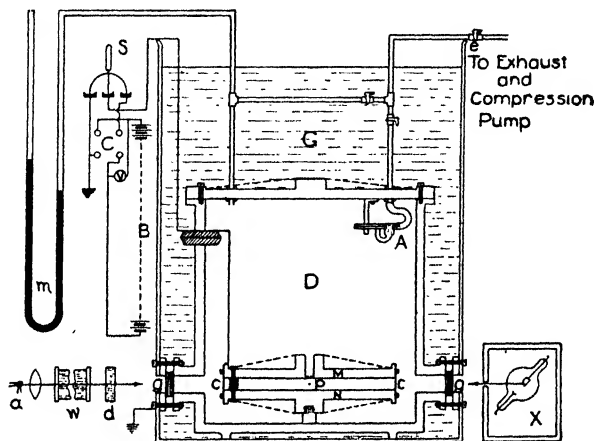

FIG. 1. Millikan's Oil Drop Apparatus

the space between the condenser plates, M and N. The hole p is then closed and the air between the plates ionized by a source of X-rays, X. Illumination is secured from the arc lamp, a, the heat rays being removed in filters w and d. The motion of the illuminated droplet is observed through a microscope fitted with an engraved scale. By collision with ions of the air the droplet acquires an electric charge, and then moves between plates M and N in a direction governed by the sign of the acquired charge and with a speed indicative of the sign of the charge carried. By reversal of the sign of the charge on M and N the direction of motion of the droplet can be reversed. In this way the droplet could be kept travelling back and forth between the plates. As a mean of 17 determinations of the times which the droplet required to fall between two fixed cross hairs in the observing telescope, whose distance apart corresponded to a distance of fall of 0.5222 cm., a value of 13.595 seconds with a maximum deviation of $\pm$ 0.2 sec. was obtained. When rising under the influence of an electric field produced by applying a potential difference of 5051 volts, the successive times required varied in the following way: 12.5, 12.4, 21.8, 34.8, 84.5, 84.5, 85.5, 34.6, 34.8, 16.0, 34.8, 34.6, 21.9 seconds. It will be seen that, after the second trip up, the time changed from 12.4 to 21.8, indicating, since in this case the drop was positive, that a negative ion had been caught from the air. On the next trip another negative ion had been caught. The next time, 84.5, indicates the capture of still another negative ion. From the

equation

$$\frac{v_1}{v_2} = \frac{m_d g}{Xe - m_d g} \quad \text{or} \quad e = \frac{m_d g}{X v_1}(v_1 + v_2), \tag{13.5}$$

where m_d is the mass of the droplet, it follows that the change in velocity produced by the acquiring of an extra charge can be given by eliminating m_d and solving the equations thus:

(a) $t = 34.8$ secs. against gravity $v_1 + v_2 = \left(\dfrac{0.5222}{13.595} + \dfrac{0.5222}{34.8} \right)$;

• (b) $t = 84.5$ secs. against gravity $v_1 + v_2 = \left(\dfrac{0.5222}{13.595} + \dfrac{0.5222}{84.5} \right)$.

The time difference between (a) and (b) is

$$0.5222 \left(\frac{1}{34.8} - \frac{1}{84.5} \right) = 0.00891 \text{ cm. per second.}$$

In this manner it was shown that successive captures of an ion effected changes in the velocity of rise against gravity respectively equal to 0.008912, 0.008911, 0.008903, 0.008883 and 0.008931 cm. per second, all of which are within $\frac{1}{5}$th of 1 per cent of the mean value of 0.00891 cm. per second. This therefore represents the change in the sum of the speeds v_1 and v_2 caused by the capture of one ion. Relationships of this sort were found to hold absolutely without exception, no matter in what gas the droplets had been suspended or what sort of droplets were used upon which to catch the ions. Experiments were conducted over five or six hours, hundreds of ions per droplet were caught and recorded by the change of speed. Here then is direct proof that the electrical charges found on ions all have exactly the same value or else small exact multiples of that value. This is the most conclusive proof of the 'atomic' structure of electricity.

From the preceding equation, with the data obtained in this study of the behavior of the oil droplets, accurate values for the ratio e/m_d could be deduced. To obtain the magnitude of the unit charge e it was necessary however to determine the mass of the droplet. For this purpose Stokes's Law could be employed to determine the radius and therefore the volume and mass of the droplet. To attain in these calculations the same high degree of precision which was obtained in the velocity determinations just recorded, Millikan found it necessary to make an investigation into the limitations of Stokes's Law with variation in the medium and with variation in the droplet size. On completion of this study, which revealed the necessity of correcting Stokes's Law for inhomogeneities in the medium—a correction which was finally made as an empirical function of the ratio of the mean free path of the gas molecules of the medium, l, to the radius of the droplet r—Millikan derived a corrected form of the Stokes equation from which the radius of the droplet was de-

termined,

$$v_1 = \frac{2}{9} \cdot \frac{gr^2}{\eta} (d_d - d_m) \left(1 + A \frac{l}{r} \right) \tag{13.6}$$

in which d_d is the density of the drop, d_m that of the medium, A an empirical constant, the other terms having the same significance as given previously. In this manner, the magnitude of e was finally obtained with a degree of precision embodied in the following expression: $e = (4.774 \pm 0.005) \times 10^{-10}$.

Subsequent research has revealed that this determination of e does not possess the accuracy indicated. The principal source of error appears to lie in the value assumed for the viscosity of air in which the droplets moved. Millikan employed a value, due to Harrington,[1] of $(1822.6 \pm 1.3) \times 10^{-7}$ c.g.s. unit. Four recent viscosity determinations indicate a value slightly over one half per cent higher. The weighted mean of these determinations, according to Dunnington,[2] gives a value of $(1832.5 \pm 1.5) \times 10^{-7}$ c.g.s. unit. With this 'high' viscosity value Dunnington deduces from Millikan's data a value for the charge, $e = (4.8059 \pm 0.0052) \times 10^{-10}$ e.s.u. More recent data of Bäcklin and Flemberg give a lower value of $(4.7941 \pm 0.0089) \times 10^{-10}$ e.s.u. and data of Ishida, Fukushima and Suetsugu give the abnormally high value of $(4.8453 \pm 0.0043) \times 10^{-10}$ e.s.u. Because of some uncertainty in the voltage calibration of this latter value, Dunnington does not include this in arriving at a weighted mean value of

$$e = (4.8036 \pm 0.0048) \times 10^{-10} \text{ e.s.u.}$$

from oil-drop determinations.

(14) **Electron Charge from Other Measurements**: It is now believed that the elementary charge e on the electron is more accurately determined by other measurements than by the oil-drop method. Actually a number of different methods have been employed to give values for the three constants, the electron charge e, the specific charge of the electron e/m and the ratio of Planck's constant, h (see Chap. II), to the electron charge, e. These interlocking determinations have, however, revealed a discrepancy between the three constants that, thus far, has not been resolved. An analysis of the data and of the discrepancy has been given in the paper of Dunnington cited above.

The value of the electron charge e obtained from measurements with X-rays and a ruled grating enjoys a high degree of confidence. The value is obtained thus: the wave length of a characteristic X-radiation is measured by use of a ruled grating.[3] The X-radiation is then employed for the determination with the aid of the Bragg equation of the grating spaces of crystals, particularly calcite, which can be obtained in a pure state and geometrically perfect (du-

[1] E. L. Harrington, *Phys. Rev.*, **8**, 738 (1916).

[2] F. G. Dunnington, *Rev. Mod. Phys.*, **11**, 65 (1939).

[3] A. H. Compton and R. L. Doan, *Phys. Rev.*, **27**, 104 (1926); J. W. duMond and V. L. Bollman, *ibid.*, **50**, 524 (1936); **54**, 1005 (1938).

Mond and Bollman, 1938). The technique of the determination is outlined by these authors as follows:

The usual procedure in determining the electronic charge e from the concordant ruled grating measurements of the X-ray wave lengths involves a measurement of the diffraction angle θ in Bragg reflection from a crystal surface and a computation of the interplanar spacing d of the crystal lattice in absolute units by means of the familiar formula (see Vol. II), with refractive index correction of Siegbahn,

$$n\lambda = 2d \sin \theta (1 - \delta/\sin^2 \theta). \qquad (14.1)$$

By such methods the absolute dimensions of the crystal lattice may be determined. If, as in the case of calcite, the lattice is not cubic, the absolute volume of the unit cell may be determined either (1) by combining the value of d with X-ray or optical goniometric measurements on a macroscopic crystal to establish the characteristic angle β of the rhombohedron or (2) X-ray determinations of the interplanar spacing may be made for several Miller indices, two being theoretically sufficient to establish the necessary angular relationships. The first-mentioned procedure is by far the most common. The absolute volume of the unit cell for calcite, generally expressed as $8d^3\phi(\beta)$, is then combined with a measurement of the macroscopic density ρ of the crystal employed and by means of the formula

$$d = (Me)^{1/3}[2F\rho\phi(\beta)]^{-1/3} \quad \text{or} \quad e = 2d^3F\rho\phi(\beta)M^{-1}, \qquad (14.2)$$

the value of e is computed. The molecular weight of the calcite is M and F is the Faraday constant. Dunnington's recent evaluation of all these factors gives a value of $e = (4.8025 \pm 0.0004) \times 10^{-10}$ e.s.u.

The specific electron charge, e/m, is determined from so-called free electron and spectroscopic determinations. In the latter the constant is deduced from the fine structure analyses of hydrogen-like pairs such as of $^1H - He^+$ and $^1H - {}^2H$ or from the Zeeman effect. The free electron measurements include determinations of linear acceleration, magnetic deflection, crossed fields and X-ray refraction. Both sets of determinations now approach concordance with each other and give as a weighted mean of 10 different sets of observations $e/m = (1.7591 \pm 0.0002) \times 10^7$ e.m.u. By substituting this value in the Rydberg equation $R_\infty = 109737.42 = 2\pi^2 e^4 m/h^3 c$ (see Chap. II) and taking the value of Planck's constant as $h = 6.610 \times 10^{-27}$ erg sec., the derived value for e becomes $(4.7963 \pm 0.0002) \times 10^{-10}$ e.s.u., significantly lower than the preceding.

From a determination of the minimum voltage V at which electrons are able to produce X-rays which can pass through a spectrometer, that is, from the limit of the continuous X-ray spectrum, the value of h/e can be deduced. The wave length λ of the X-radiation is measured with a ruled grating and the determination of h/e follows immediately from the relation $hc/\lambda = Ve$. Dunnington's analysis of the best data gives a weighted average of $h/e = (1.3763 \pm 0.0003) \times 10^{-17}$ e.s.u. Combination of this with the same value

(18) **The Size of the Electron:** It can be shown in a number of ways that the energy of an electron is given approximately by the expression e^2/r where r is the radius of the electron of charge e. By the special theory of relativity, this energy is related to the mass by the approximation

$$e^2/r \sim mc^2,$$

so that the radius of the electron, at least as to order of magnitude, is given by the expression $r = e^2/mc^2$ which with the data of preceding sections is approximately 2.8×10^{-13} cm. It is important to note that this is an entirely lower order of magnitude than the atomic radius which, as will be shown (Vol. II), approximates to 10^{-8} cm.

(19) **The Wave Theory of the Electron and of Matter:** The atomistic concept of matter and also of electricity as developed in the study of the electron contrasted with the undulatory theory of heat and light energy which was the basis of nineteenth century physics. The early years of the present century brought, however, a revolutionary change in the concept of energy. Energy as a continuum was found by Planck in 1900 to be inadequate to account for the facts of black-body radiation. He therefore proposed his hypothesis of discontinuous emission of radiation. In 1902, the investigation of the photo-electric effect by Lenard led to the astonishing result that electrons, liberated from metal plates by ultra-violet light, had velocities which were independent of the intensity of the light, but dependent on the frequency of the light, increasing in velocity with increase of the frequency. If the electronic velocities were measured by the potential V required to prevent all the liberated electrons from leaving the illuminated plate it was found that V varied linearly with the frequency of the light

$$V = C\nu - V_0, \tag{19.1}$$

where C is a positive constant independent of the metal and the same for all metals, V_0 is a constant characteristic of the metal. If equation (19.1) be multiplied be e, the electronic charge, and rearranged it follows that

$$e(V + V_0) = Ce\nu. \tag{19.2}$$

Since eV is an energy quantity, being the kinetic energy of the electrons leaving the plate with the highest velocity, it follows that the product $Ce\nu$ must also have the dimensions of energy. The frequency ν has the dimensions of reciprocal time. Hence, Ce must have the dimensions of a product of energy and time, that is the dimensions of what is known in mechanics as *action*. As C is a universal constant and e also, the product Ce must also be a universal constant. If we assign to it the symbol h, the measurements of the photo-electric effect show it to have the magnitude

$$h = 6.62 \times 10^{-27} \text{ erg sec.}$$

The product $h\nu$ represents a quantum of energy, the smallest unit of energy of

the given frequency involved in energy change upon the Planck hypothesis. The relationship between the electronic velocities and the frequency of the radiation may be expressed by means of the equation,

$$\tfrac{1}{2}mv^2 \; = \; Vc \; = \; h\nu \; - \; h\nu_0. \tag{19.3}$$

The quantity $h\nu$ measures the energy absorbed by the electron from the radiation; $h\nu_0 = eV_0$ is the work necessary to get the electron through the surface. The potential difference V_0 is known as the 'work function' for electrons passing through the surface.

The concept of individual light quanta, each with energy equal to the product of the frequency and the quantum of action, h, was definitely proposed by Einstein in 1905 and became the fundamental idea in all questions involving the interactions of light energy and matter. It provided the basis for the modern treatments of photochemistry, photoelectric and spectroscopic studies including fluorescence and chemiluminescence, and for the Bohr theory of spectra and the structure of the atom. The extraordinary development which this phase of atomistics has undergone is set forth in detail in Chapter II.

Progress in the quantum theory of energy made familiar the concept of units of energy, light quanta or photons, with the atomistic, discontinuous, discrete structure hitherto characteristic of matter. The reversal of this mode of thought, the concept of material particles with the wave nature of light was proposed in 1924 by Louis de Broglie. It led to the wave mechanics of Schrödinger and to the quantum mechanics of Heisenberg, two apparently different but, in reality, complementary aspects of a general wave theory of matter. This theory assigns to each material particle a wave of characteristic wave length bearing the same relation to its mass and velocity as was found by quantum theory for the photons. The relation may be expressed in the equation

$$\lambda \; = \; h/mv, \tag{19.4}$$

where λ is the wave length of the particle with mass m and velocity v, h being again Planck's constant.

It is of interest to point out the significance of this equation when applied to the electron. From the data already considered, for the electron h/m has the value 7.27. For electrons having velocities in the range 10^7 to 10^9 cm. per sec., the de Broglie equation indicates that such electrons should have wave lengths of the same order of magnitude as X-rays. Herein lay the possibility of experimental test using the same methods of measurement as are employed with X-rays using crystals (Vol. II).

Such a test was applied successfully by Davisson and Germer in 1927. They showed that a stream of electrons emitted from a hot filament was selectively reflected from a single crystal of nickel in a manner entirely analogous to the reflection of X-rays. The intensity of the reflection in a given direction was governed, as with X-rays, by the lattice structure of the crystal. G. P. Thomson, independently and in the same year, provided additional evidence

for the wave nature of the electron by passing a stream of accelerated electrons, at potentials from 20,000 to 50,000 volts through thin films of metal, and determining the diffraction patterns produced by the action of the diffracted electrons on a photographic plate. The radius of the diffraction ring r produced was found to be proportional to the wave length λ of the electrons diffracted, the applied voltage determining the velocity and, hence, the wave length of the electron according to the de Broglie equation.

With these experiments the corpuscular and undulatory aspects of both matter and energy became apparent. Later experiments, notably those of Stern,[1] extended the wave structure of matter to particles of atomic dimensions by showing that hydrogen and helium could be made to produce diffraction patterns. The particulate and wave aspects of matter emphasize the energy, momentum or speed of the unit on the one hand or the determination of position in time on the other. These aspects of matter are to a degree mutually exclusive as expressed in the uncertainty principle enunciated by Heisenberg (1927). This principle which now forms one of the fundamental bases of modern physics in its dualistic approach to matter and energy emphasizes that the simultaneous determination of velocity (or its related properties of energy or momentum) and position is not possible. The degree of uncertainty is expressed by the equation

$$\Delta x \cdot \Delta p \approx h, \qquad (19.5)$$

where h is Planck's constant, Δx is the uncertainty in the determination of the position and Δp the uncertainty in the measurement of the momentum $p = mv$. Great precision in the determination of this latter produces a correspondingly larger uncertainty in the definition of position and vice versa. The principle indicates that the wave and particle aspects of matter are complementary. In both physics and chemistry, depending upon the nature of the objective, one or other of the aspects of the material system will be emphasized to the subordination of the other.

(20) **The Inter-relation of Mass and Energy:** The relativity expression for the mass of a particle in terms of its velocity $m = m_0/(1 - v^2/c^2)^{1/2}$ involves as a consequence a direct relation between mass and energy. The increase in kinetic energy dE resulting when a force F acting on a body moves through a distance dx is equal to Fdx. If, for the force F, the rate of change of momentum be substituted then

$$dE = d(mv)/dt \cdot dx. \qquad (20.1)$$

Since the velocity v of the particle is dx/dt the expression takes the form

$$dE = vd(mv) = v^2 dm + mvdv. \qquad (20.2)$$

The relativity expression for velocity in the form $m^2(c^2 - v^2) = m_0^2 c^2$ gives on differentiation

$$(c^2 - v^2)dm - mvdv = 0. \qquad (20.3)$$

[1] I. Estermann, R. Frisch and O. Stern, *Z. Physik*, **73**, 348 (1932).

From this expression it follows, by combination with (20.2), that

$$dE = c^2 dm. \tag{20.4}$$

This relation may be extended to all forms of energy such that, quite generally,

$$E = mc^2, \tag{20.5}$$

where c is the velocity of light in cm./sec., energy being expressed in ergs and mass in grams. This is the generalized law which governs all mass-energy relations.

The law of conservation of mass was formulated by Lavoisier upon the basis of his own experimental measurements. It received its most critical experimental test when applied to ordinary chemical processes in the closing decade of the 19th century and the first decade of the present century at the hands of Landolt.[1] He determined the masses of various reacting systems before and after reaction in closed glass vessels. The masses of reagent approximated 300 g. and could be weighed to an accuracy of several thousandths of a milligram. The greatest precautions were necessary to eliminate errors due to changes in absorbed moisture, in the volume and temperature of the reaction system. The reactions studied were metatheses as, for example, $HIO_3 + 5HI = 3I_2 + 3H_2O$, the majority in aqueous solutions. Of approximately fifty different experiments approximately one half showed a slight gain, the others a slight loss, all the differences lying, however, within the limits of error of ± 0.03 mg. This signifies that, in such chemical processes, the law of conservation of mass holds to within an error of 1 part in 10^7.

According to the mass-energy relationship just established, $E = mc^2$, for a reaction involving the evolution of 10^4 calories per mole, the system should suffer a loss in mass of $10^4 \times 4.2 \times 10^7/9 \times 10^{20} =$ ca. 0.5×10^{-9} g. per mole. It is thus evident that, for a system of mean molecular weight of 100 g., the occurrence of a chemical reaction involving 10 kcal. per mole is constant in weight to within 1 part in 5×10^{10}. The Landolt experiments attained a precision some 1000 times less than would have been necessary to detect such changes in mass. It is further evident, however, that, in the nuclear reactions now attainable and involving energy changes corresponding to millions of electron-volts (M.e.v.), changes in mass, readily detectable by modern precision measurements, will occur. These changes are related to the energy changes by the Einstein relation which becomes therefore the basis for a comprehensive principle of conservation, that of energy and mass, regarded as equivalent one to another, and related by the expression $E = mc^2$.

(21) **The Positron or Positive Electron:** The unit of negative electricity suggests at once the possible existence of a corresponding unit of positive electricity. Search for such originally only yielded evidence for massive positively charged particles, the positive ions, of which the lightest was the

[1] H. Landolt, *Berl. Ber.*, 301 (1893); 266 (1906); 354 (1908); also, Über die Erhaltung der Masse bei chemischen Umsetzungen, *Abh. K. Preuss. Akad. d. Wissensch.*, 1910.

hydrogen ion or proton. The search for units of positive electricity corresponding to the electron was stimulated by the relativistic wave theory formulated by Dirac in 1928. In 1932, through the experiments of Anderson, this search was brought to a successful conclusion. It was known that cosmic rays produced high velocity electrons upon impact with matter. In studying the properties of these electrons in a Wilson cloud chamber, arranged between the poles of a powerful electromagnet, and containing a lead plate 6 mm. in thickness in the center of the chamber, Anderson [1] observed, in one of the cloud photographs, that the particle producing the track must have carried a positive charge. The curvature of the track being less above the lead plate than below, it was evident that the particle travelled upwards in making the track. The direction of the curvature with a known disposition of the poles of the magnetic field established the positive charge of the particle. The length of the track after leaving the lead plate indicated decisively that the particle could not be a proton; since the length was ten times as great as the length of a proton track of the given curvature. This definitely suggested a positively charged particle of much smaller mass than the proton, the thickness of the track suggesting a particle of mass approximately that of the electron. It was, in fact, a 63 million volt positron. Anderson's observations were rapidly confirmed by Blackett and Occhialini [2] in a vertical cloud chamber in a magnetic field and in which the cosmic rays operated, through a relay, the expansion mechanism and the photographic mechanism recording the track produced.

Other methods of producing the positron and the detailed account of its properties will be discussed in the later sections dealing with nuclear processes. It will suffice here to observe that the positron, in contrast to the electron, is very short-lived. Within a period of the order of 5×10^{-10} sec. it will have lost the greater part of its kinetic energy and is then annihilated by interaction with an electron with the simultaneous production, to conserve momentum, of two X-ray photons whose joint energy, from the considerations advanced in Section (20) must be approximately 1 M.e.v. Experiments of Chao [3] and of Gray and Tarrant [4] demonstrated the existence of a secondary isotropic radiation with an energy of about 0.5 M.e.v.

(22) **The Investigation of Atomic Architecture**: The methods employed for exploring the architecture of the atom consist in determining the influence of the atomic constituents of a molecule on various impinging radiations. Lenard and his co-workers examined the scattering of beams of electrons by atoms. It was found that swift electrons (cathode particles) encountered little resistance in their passage through atoms which behaved as though they were largely transparent to such impinging particles. Massive atoms with a radius of $\sim 10^{-8}$ cm. would be practically impenetrable to electrons. It was these experiments which suggested to Lenard a concept of an atom with a small

[1] C. D. Anderson, *Science*, **76**, 238 (1932); *Phys. Rev.*, **43**, 491 (1933).
[2] P. M. S. Blackett and P. S. Occhialini, *Proc. Roy. Soc.*, [A], **139**, 699 (1933).
[3] Chao, *Proc. Nat. Acad. Sci.*, **16**, 431 (1930); *Phys. Rev.*, **36**, 1519 (1930).
[4] Gray and Tarrant, *Proc. Roy. Soc.*, [A], **136**, 662 (1932); **143**, 681 (1934).

impenetrable center surrounded by a cloud of electrons, this latter offering but little resistance to the passage of swiftly moving electrons.

The quantitative development of the concept of the nuclear atom is due to Rutherford who, in 1911, initiated experiments on the scattering of α-particles by atoms. Owing to their great mass relative to the electrons, α-particles are uninfluenced by the electrons with which they come in contact. They are, however, stopped or deflected by the more massive positive nuclei of the atoms through which they pass.

Proof of the minuteness of the atomic nuclei is obtained by a study of the tracks of the α-particles and β-particles or electrons through gases. Photographs of such tracks are obtainable since the gas through which the particles pass is ionized and the ions may be rendered visible by the condensation of water vapor upon them. This is the technique of the Wilson [1] cloud chamber. Study of photographs so obtained shows that a β-particle may pass through as many as 10,000 atoms before it comes near enough to an electronic constituent of any of the atoms to detach it from its system and form an ion, a circumstance indicative of the relative freedom of the atomic space from such electronic constituents. The cloud photographs reveal, on the other hand, that, on the average, an α-particle passes through 200,000 atoms without approaching near enough to the nucleus to suffer appreciable deflection. This leads to the conclusion that the positive nucleus is but a minute fraction of the total atomic volume.

(23) **The Nuclear Charge:** The number of free positive charges on the nuclei of atoms were defined by studies of Rutherford and his co-workers on the scattering of α-particles in passing through various metal foils. The effective deflecting force causing the scattering of an α-particle of charge $2e$ by a massive atom of charge Ze is the coulomb force $2Ze^2/r^2$ where r is the distance separating the nuclei. The orbit of the α-particle is therefore a hyperbola with the nucleus, of charge Ze, as the focus. According to Rutherford, with an incident ray containing one α-particle per sq. cm., the number of particles, $n(\phi)$, per unit solid angle which suffer a deflection ϕ is given by the expression:

$$n(\phi) = Z^2 \left(\frac{m}{M} \right)^2 \left(\frac{e^2}{mc^2} \right)^2 \frac{1}{(v/c)^4 \sin^4 (\phi/2)}, \qquad (23.1)$$

where m and M are the masses of the electron and the α-particle and v is the velocity of the α-particle at great distance from the nucleus, when its energy is entirely kinetic.

The distribution of the scattered α-particles is determined by projecting a stream of α-particles normally to a thin metal foil and counting scintillations produced on a fluorescent screen located at various positions on a circular arc centered at the scattering foil. For scattering in gases, the distribution is determined by photographing, simultaneously from two directions, a large

[1] C. T. R. Wilson, *Proc. Camb. Phil. Soc.*, 9, 333 (1897); *Phil. Mag.*, 7, 681 (1904).

number of tracks made visible by the cloud-chamber expansion method, measuring the angles of deflection produced. The original measurements of Rutherford [1] in 1911 and the subsequent determinations of Geiger and Marsden [2] in 1913 showed that the distribution function had the form deduced theoretically. They employed indirect methods for determining the number of α-particles falling per unit of time on the metal foil. The uncertainty thus introduced caused an uncertainty in the determination of Z for gold amounting to 20 per cent. Chadwick [3] later extended the measurements to platinum, silver and copper foils using an indirect and more accurate method of measuring the number of α-particles in the primary stream. A known fraction of these were counted by scintillations produced upon the fluorescent screen in the path of the primary stream, the fraction in question being secured by rotating a disc with a narrow slit between source and screen. C. T. R. Wilson, using fast electrons, employed the cloud chamber method to determine the fraction scattered through 90° by air assuming the correctness of the distribution function. P. M. S. Blackett [4] subsequently confirmed this assumption using both argon and air, a conclusion independently verified for argon by Auger and Perrin.[5]

The conclusion initially reached in these scattering experiments was that the nuclear charge was approximately equal to one-half the atomic weight. This conclusion agreed with earlier work by Barkla [6] on the scattering of X-rays. This work indicated that, in each atom, the number of scattering centers, namely, the electrons, was approximately equal to one-half the atomic weight. As is now well known, the charge Z on the nucleus and the number of extra-nuclear electrons are equal and the number is known as the atomic number. It is of interest to compare the results of the scattering experiments with the known data for the atomic numbers. These are shown in the following table:

TABLE III

Nuclear Charges from Scattering Experiments

Element	Atomic Number	Z	Investigator
Pt	78	77.4 ± 1	Chadwick
Ag	47	46.3 ± 0.7	"
Cu	29	29.3 ± 0.5	"
Au	79	79 ± 2	Rutherford and Chadwick
A	18	19	Auger and Perrin
Air	6, 7	6.5	C. T. R. Wilson

[1] E. Rutherford, *Phil. Mag.*, **21**, 669 (1911).

[2] H. Geiger and E. Marsden, *ibid.*, **25**, 604 (1913).

[3] J. Chadwick, *ibid.*, **40**, 734 (1920).

[4] P. M. S. Blackett, *Proc. Roy. Soc.*, [A], **102**, 1 (1922).

[5] P. Auger and F. Perrin, *Compt. rend.*, **175**, 340 (1922).

[6] C. G. Barkla, *Phil. Mag.*, **21**, 648 (1911).

In the work of Geiger and Marsden, experiments with Pt, Ag, Cu, Al and Sn showed that the Z values were within 5 per cent of the accepted atomic numbers if the value of Z for gold was taken as 79.

(24) **The Atomic Number:** The actual count, with precision, of the extra-nuclear electrons in elementary substances was accomplished by Moseley, 1914.[1] The suggestion of Laue, 1912, that the regular spacing of atoms in a crystal could be utilized, on the principle of a grating, for the analysis of short wave-length ether waves, had been translated into actual practice by the Braggs,[2] an X-ray spectrometer devised and the wave lengths of various X-rays determined.   Moseley, in 1914, utilizing a wide variety of elements as targets in the X-ray bulb, found that, in addition to general X-radiation which all emitted, each element emitted X-radiations characteristic of the given element. As the voltage over an X-ray tube is raised above a certain definite value, the anti-cathode is observed to emit an X-radiation which is characteristic of the
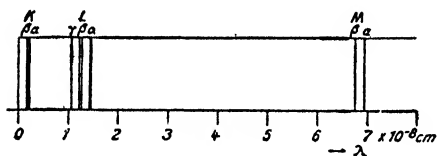
FIG. 2. K, L, M, etc., Series

material of the target and which is much more intense than the continuous radiation.   For each element it is thus possible to obtain a series of monochromatic X-radiations. These rays as shown in Fig. 2 (which is a typical spectrum) are classified according to their wave lengths into K, L, M, etc.

Moseley carried out an investigation in which he measured the wave lengths of the lines in the K and L series for most of the elements.   He found that the spectra of the different elements, beginning with that of aluminum, and ending with that of gold, could be arranged in the same order as in the periodic table, and that under these conditions the wave length of any one characteristic line of the K or L series decreased regularly with increase in the ordinal number of the element in the table.   Furthermore, Moseley found that if he assigned to each element a number, Z, corresponding to its place in the periodic table (Al = 13, Si = 14, etc., as far as Au = 79), there exists for each type of radiation a simple relation of the form

$$\sqrt{\nu} = a(Z - Z_0), \qquad (24.1)$$

where ν is the frequency, and a and Z_0 are constants.

These measurements have been repeated and extended by de Broglie, A. W. Hull and M. Siegbahn.[3]   Fig. 3 shows the K series for some of the elements between As and Rh as photographed by the latter.   The dark line on the extreme left hand corresponds to a wave length zero.   The first line in each spectrum is found on closer examination to consist of two lines very close

[1] *Phil. Mag.*, **26**, 1024 (1913); **27**, 703 (1914).

[2] X-rays and Crystal Structure, 1915.

[3] M. Siegbahn has reviewed the observations on X-ray spectra and their relation to Moseley's law in *Jahrb. d. Rad. u. Elektronik*, **13**, 296 (1916).

together. These are known as the α_2 and α_1 lines of the K series. The darker lines to the right may also be separated into two lines, known as the β_1 and β_2 lines of the K series. Now the significance of Moseley's law is this: If we plot the square roots of the frequency, or (what amounts to the same thing) the values of $\sqrt{1/\lambda}$ for any one of these lines, as ordinates against the ordinal number Z, we obtain a straight line for each of these characteristic radiations,
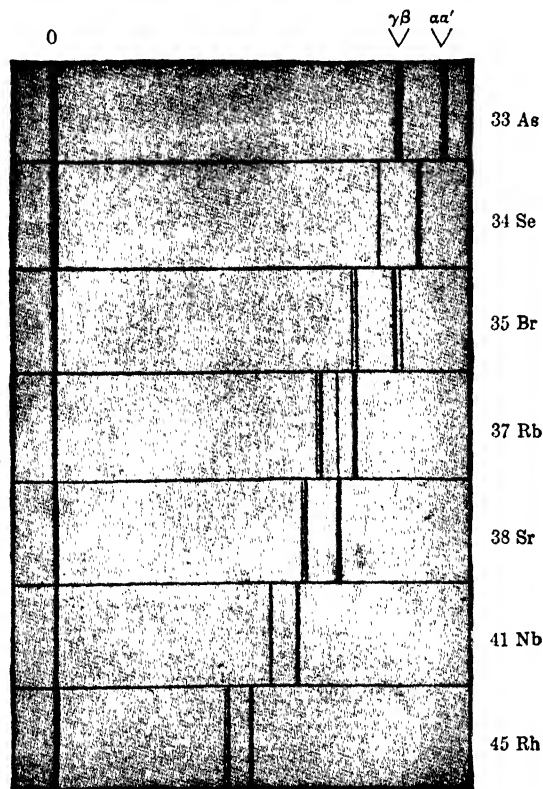

FIG. 3. *K* Series for Elements As–Rh

as shown in Fig. 4. The value of Z thus determined is known as the *atomic number*.

The order of increasing frequency was that of the elements arranged in the order of their atomic weights with conspicuous and significant exceptions. A missing element in the periodic order gave a missing step in the increment of the square root of the frequency. In the whole series of elements ranging from hydrogen = 1 to uranium = 92, six such gaps were found indicating that six elements were still unknown in this interval. In 1923, Hevesy and Coster

discovered Hafnium, No. 72.   In 1925 Noddack announced the discovery of Masurium No. 43, and Rhenium No. 75.   This was followed by intensive study of this latter.   In 1926, Hopkins indicated the possible presence of Illinium, No. 61, in association with other rare earth elements.   Since then, through the contributions of workers in induced radioactivity (see Section 57) the periodic system of the elements has been completed and the properties of the next higher element, No. 93, have been defined.   Element No. 87, has been found by Mlle. Perey [1] as a rare branching product in the natural radioactive
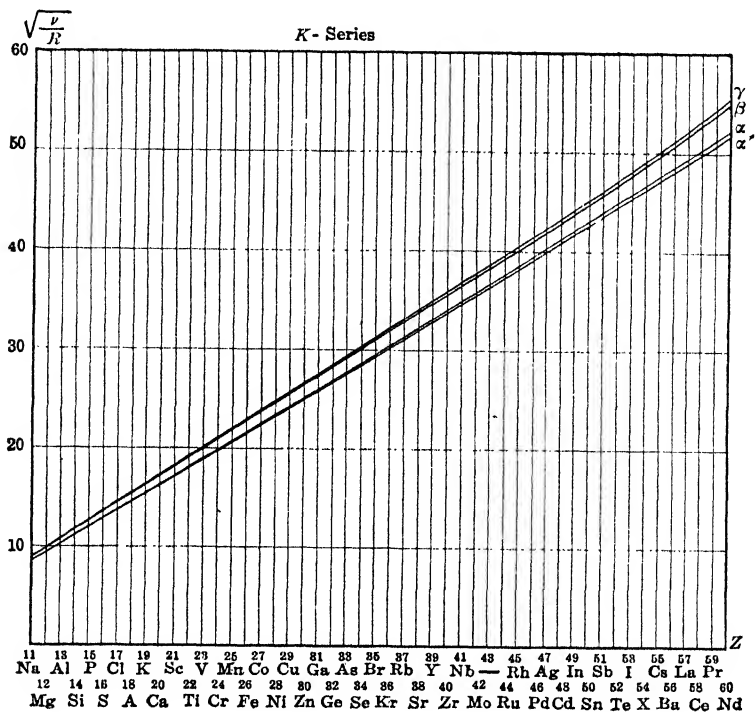
FIG. 4.   Relation between Atomic Number and Frequency

actinium family (Section 31).   Perrier and Segrè [2] found No. 43, the masurium of Noddack, among the products of neutron and deuteron bombardment of molybdenum.   Most of its characteristics resemble rhenium very closely and Noddack's method of enriching rhenium should also have concentrated No. 43. The rare earth element, No. 61, has probably been produced by deuteron bombardment of neodymium but no chemical studies are available.[3]   In

[1] Mlle. Perey, *Compt. rend.*, **208**, 97 (1939).

[2] Perrier and Segrè, *Nature*, **143**, 460 (1939).

[3] Pool and Quill, *Phys. Rev.*, **53**, 437 (1938).

1940 the final missing element, No. 85, was prepared by alpha-particle bombardment of bismuth.[1]   It is much more metallic than iodine but is accumulated, like iodine, in the thyroid gland.   It is radioactive, with a half-life of 7.5 hours and emits two ranges of α-particles, 6.5 and 4.5 cm. respectively. Element No. 93 is the only certainly known member of the trans-uranium series and arises from neutron bombardment of uranium, which also results however in nuclear fission (Section 63).

Since the X-ray frequencies involved in Moseley's investigations are probably due to vibrations arising from electrons proximate to the nucleus, the additivity of the square root of the frequency, observed by Moseley, indicates or suggests that the charge on the nucleus in a given element differs from that of the nucleus of the preceding element in the periodic classification by a constant and definite charge.

(25) **Nuclear Constitution:** The nucleus, according to the views just developed, possesses a positive charge equal to the atomic number and equal and opposite to that of the extra-nuclear electrons whose number is therefore also determined by the atomic number.   The mass of the atom, save for the minor amount associated with the extra-nuclear electrons, is also concentrated in the nucleus.   If this nuclear mass were to be ascribed to constituent protons, the number of positively charged protons in a nucleus would be given by the atomic weight A of the atom.   Since the atomic weight is greater than the atomic number or net nuclear charge Z, it was suggested that the nucleus might also contain electrons, $A - Z$ in number.   The stability of such systems was, however, regarded as extremely doubtful.

Rutherford, in 1920, had suggested that, in addition to protons, particles might also exist having unit mass but no electric charge.   To these possible particles he gave the name neutrons.   With such particles, the characteristics of the nucleus as to charge and mass could be accounted for on the assumption that the nucleus contained Z protons and $A - Z$ neutrons.   With such a structure the stability of the nucleus would become more understandable. Indeed the possibility would exist of an increased stability due to a rapid, continuous resonating exchange of positive charge between proton and neutron. Experimental proof of the existence of such neutral primary particles was furnished in 1932, by J. Chadwick, as products of bombardment of light elements by α-particles.   The details of their discovery, their methods of preparation and the properties of neutrons will be deferred to the discussion, later, of nuclear processes.   As a preliminary to such a discussion, the phenomena of radioactivity must first be detailed.   From such data, our present knowledge of nuclear constitution has been largely derived.

(26) **Radioactive Disintegration:** The phenomenon of spontaneous disintegration in the radioactive substances discovered by Becquerel, Pierre and Marie Curie (1896–1898) is to be attributed, on the basis of the Rutherford nuclear atom, to an instability of the nucleus.   Three types of radiations were

---

[1] Corson, Mackenzie and Segrè, *Phys. Rev.*, **57**, 459 (1940); **58**, 672 (1940).

rapidly recognized by reason of their behavior under the influence of a magnetic field, the α-particles carrying a positive charge, β-particles having a negative charge and γ-rays uninfluenced by the applied field.

α-Particles: From deflection experiments, under the influence of known electrical and magnetic fields analogous to those employed in the case of cathode particles, it was shown that the value of e/m for the particles corresponds to that of a doubly ionized helium atom. That the particle was in fact such and not a singly charged particle of mass 2 was made probable by the observation of Rutherford, Ramsay and Soddy that radioactive substances develop helium. This was decisively demonstrated by the experiment of Rutherford and Royds [1] who showed that a thin-walled glass vessel containing the radium emanation, and sufficiently thin to permit the passage of α-particles through the glass wall,

FIG. 5.   The Distribution of Ionization

yielded, when the surrounding volume had been evacuated, a gas easily recognizable as helium by spectroscopic observation.

The deflection experiments also showed that the initial velocity of the emitted α-particles was a constant and characteristic of the element emitting. This velocity may be expressed in terms of the range of the α-particles or the total distance it will traverse in a gas. This range is inversely proportional to the pressure; that is to say, the number of molecular encounters necessary to exhaust the kinetic energy of the particle is constant for a given gas. The reciprocal of the range is termed its *stopping power.* In its passage through the gas the α-particle removes electrons from the gas molecules thus producing ionization. The distribution of ionization along the path is not constant but varies in the manner indicated in Fig. 5 for an α-particle from RaC' with a range of 6.6 cm. in air at 0° and 760 mm. For α-particles with smaller initial velocities the path is the same, beginning at the corresponding point in the path. An empirical relationship, found by Geiger, connects the range R_0 in air at 0° and 760 mm. with the initial velocity v of the α-particle:
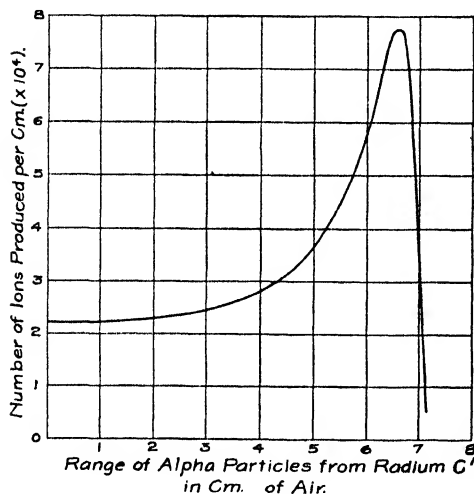
$$v^3 = 1.08 \times 10^{27} R_0.$$

The scintillations produced by α-particles on phosphorescent screens, for

[1] E. Rutherford and T. Royds, *Phil. Mag.*, 17, 281 (1909).

example of zinc sulfide, may be utilized to determine the number of α-particles emitted from a given source. The number of scintillations produced per unit of time on a known area of the screen, e.g., 1 mm.^{2}, are counted with the aid of a microscope and, from the geometry of the source and screen, the number of particles emitted can be calculated. Another method, introduced by Rutherford and Geiger, and developed by the latter, measures the number of α-particles emitted, by the ionization produced in a chamber on entry of an α-particle, the ionization producing a break-down of potential between a metallic point within the chamber and the chamber wall. The apparatus has now become familiar in various forms as the 'Geiger counter.'

β-Particles: These are swift electrons emitted by the nucleus with velocities in some cases approaching that of light. In the case of RaC some of the particles have a velocity equal to $0.998c$. Their electronic nature is readily established by deflection measurements of their velocity and of the ratio e/m. The number of particles emitted can be ascertained by Geiger counter measurements. Owing to their small mass, compared with α-particles, they have much less kinetic energy and consequently a smaller ionizing power. They are more easily deflected and their cloud-track in the Wilson chamber will therefore be more tortuous than that of the α-particle. A β-particle of velocity $0.9c$ produces in air about 55 ions per centimeter of path or about $\frac{1}{200}$ the ionization of an α-particle.

The high velocity of β-particles is unfavorable for loss of energy through ionization. Consequently β-particles are more penetrating than α-particles and follow a different absorption law. They do not all complete a path of the same length but are successively stopped according to an exponential law, according to the equation

$$I = I_0 e^{-\mu d}$$

in which I_0 is the initial intensity of β-particles, I the intensity after passing through a thickness d in an absorbing medium with an absorption coefficient μ. The half value layer $d_{0.5}$ is given by the expression $\mu = \ln 2/d_{0.5} = 0.693/d_{0.5}$ cm.$^{-1}$. The absorption coefficient is normally expressed in terms of aluminum foils as the absorption medium. The following table lists some typical coefficients and half value thickness.[1]

TABLE IV

ABSORPTION COEFFICIENTS OF β-PARTICLES

Element	μ cm.$^{-1}$ Al	$d_{0.5}$ cm. Al
UX$_1$	460	1.51×10^{-3}
UX$_2$	18.2	3.8×10^{-2}
Ra	312	2.2×10^{-3}
RaB	13; 77; 890	$5.3 \times 10^{-2}; 9 \times 10^{-3}; 8 \times 10^{-4}$
RaC	13.5; 50	$5.1 \times 10^{-2}; 1.3 \times 10^{-2}$
RaD	5500	1.2×10^{-4}
RaE	43	1.6×10^{-2}

[1] Meyer and Schweidler, Radioaktivität, Teubner, Berlin-Leipzig, 2nd ed., 1927.

γ-*Rays:* These are electromagnetic waves travelling with the velocity of light with wave lengths characteristic of the emitting source. The rays are 'harder' even than the X-rays with wave lengths down to 10^{-11} cm. The crystal lattice method employed for X-rays may be successfully applied to the 'softer' γ-rays down to wave lengths of 5×10^{-10} cm. The harder rays are too short to produce good interference phenomena.

The law of absorption for a homogeneous bundle of γ-rays is exponential as with β-particles but the absorption coefficient μ is much smaller for γ-rays. The half layer, $d_{0.5}$, in a given material is, consequently, much greater. For example, with lead, the value for $d_{0.5}$ is 0.5 mm. for the most penetrating β-particles and 14 mm. for the hardest γ-rays. The absorption coefficient varies approximately with the density.

The γ-radiation from a given source is not always homogeneous and it varies from source to source. This is shown by the following table of absorption coefficients in aluminum.

TABLE V

ABSORPTION COEFFICIENTS OF γ-RAYS IN ALUMINUM

Radio-element	μ_γ cm.$^{-1}$
Ra	354, 16.3, 0.27
RaB	230, 40, 0.57
RaC	0.23, 0.127
ThB	160, 32, 0.36
Ms Th$_2$	26, 0.116
Io	1088, 227, 0.408

γ-rays produce ionization. This is largely due to the electrons set free with sufficient velocity to ionize gas molecules along their paths. The number of ions produced by the γ-radiation of RaC is approximately equal to that of the β-particles. Owing, however, to the much longer paths of the γ-rays the ionization per cm. of path is much smaller than in the case of β-particles.

(27) **The Velocity of Radioactive Change:** The fundamental law governing the rate of radioactive transformation states that the number of atoms disintegrating per unit time, $- dN/dt$, is proportional to the number of atoms N of the given kind which are present. If λ is the constant of proportionality, the *radioactive decay constant*, then it follows that

$$- dN/dt = \lambda N.$$

Upon integration there results the expression

$$N_t = N_0 e^{-\lambda t},$$

where N_0 is the initial number of atoms of one kind present (or quantity measured in any other units), N_t the number remaining after any interval of time t. The rate has been found to be independent of the external conditions, physical and chemical, that have, so far, been imposed. The fraction λ changing per

unit of time is the reciprocal of the average life θ of the atoms of a given species. The half-life period, $t_{0.5}$, of a given radioactive element is the time required for half of any given quantity to undergo change.

$$t_{0.5} = \theta \ln 2 = \ln 2/\lambda = 0.693/\lambda.$$

This half-life period is the most fundamental and characteristic constant of a radioactive species. The different periods among the various radioactive elements embrace a range from 10^{-11} seconds to 10^{10} years.

The law of transformation is a statistical law. It implies that each atom has the same disintegration probability. The statistical aspect of the law is confirmed by the observation that there are fluctuations about the mean number of particles emitted per unit time and that these fluctuations obey statistical laws.

(28) **Radioactive Equilibrium:** The rate at which one element changes into another or the relative periods of the members of a radioactive series of elements evidently control the quantities of the elements that can coexist. The shorter the life of a given element, the smaller the quantity that can coexist with its parent or offspring elements. The relations which exist may be variously classified according to the genetic distribution of elements with different life periods. One of the simplest and most important cases is that of a long-lived parent succeeded by a much shorter one. The latter will accumulate until the rate of its decay just counterbalances its rate of formation, when an irreversible dynamic equilibrium results—called radioactive equilibrium. For the case of a long-lived parent A_1 with period λ_1 of which N_1 atoms are present, the equilibrium quantities of element A_2, A_3, etc., are given by

$$\lambda_1 N_1 = \lambda_2 N_2 = \lambda_3 N_3 = \cdots, \tag{28.1}$$

or

$$\frac{\lambda_1}{\lambda_2} = \frac{N_2}{N_1}, \text{ etc.} \tag{28.2}$$

Thus, the equilibrium quantities are inversely proportional to the fraction λ. This is a principle of first importance, since it means that only long-lived elements can be accumulated in large quantities and vice versa.

Another principle of importance in connection with radioactive equilibrium is one which for convenience may be termed "constant flux" of atoms. It follows directly from the definition of radioactive equilibrium that, in a series in equilibrium, the number of atoms of each kind undergoing change in unit time must be a constant. Since one α-particle (or β-particle) is emitted per atom changing, the number of α-particles emitted per second is constant for equilibrium quantities of all the elements in a series. It is therefore evident that much simplicity is effected by choosing a gram of one member in a series as the quantity unit and letting the quantities of other members of the series in equilibrium with 1 gram of the standard be designated by a common unit. It

must be understood that these simple relations hold only in a straight series, where no branching occurs.[1]

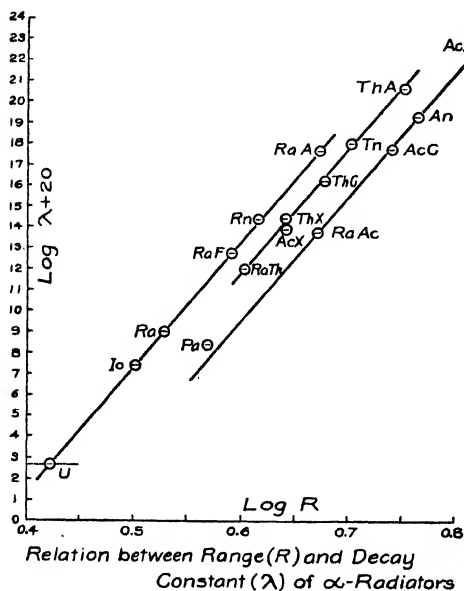(29) **The Geiger-Nuttall Relation:** A purely empirical relation was discovered by Geiger and Nuttall [2] which has been of great practical service.   They observed that the more rapid the rate of decay of an α-radiator the greater the range of the α-rays.   If $\log \lambda$ (where λ is the decay constant) be plotted against $\log R$ (the range), a straight line results. As will be seen from Fig. 6, the lines have the same slope for all three of the radioactive series.   The equation is: $\log \lambda = A + B \log R_0$, where A is a constant characteristic of each series, with the value -37.7 for the uranium series; B has the same value for all of the series -53.9; R_0 is the air range at $0°$ and 760 cm.   The element AcX is an exception to this rule.

This empirical rule has been of great use in calculating the immeasurable short periods of the long-range α-radiators.   It

Relation between Range(R) and Decay Constant (λ) of α-Radiators

Fɪɢ. 6

has recently become possible to attack the problem of the theoretical significance of the relation; evidently, it may be expected to have a profound relation to the structure of the nucleus and to the instability of the nucleus as illustrated by α-ray emission.

(30) **The Gamow-Gurney-Condon Theory:** The explanation of the Geiger-Nuttall relation was given simultaneously in 1928 by Gamow and by Gurney and Condon.   A stable atomic or molecular system may be regarded as occupying a minimum in a potential energy surface as indicated in Fig. 7.   The ordinates refer to the potential energy of the system, the abscissae to some interatomic or intermolecular distance.   For a radioactive atom the distance $r = 0$ represents a stable nucleus, r representing the distance between the disintegration products, say an alpha-particle and the residual nucleus.   The form of the outside walls of the potential energy crater is known from scattering experiments with α-particles since these show that Coulomb's Law holds down to distances of the order of 10^{-12} cm. at least.   Since the charge on a helium

---

[1] N. E. Dorsey, *J. Wash. Acad. Sci.*, **11**, 381 (1921).

[2] Geiger and Nuttall, *Phil. Mag.*, **22**, 613 (1911); **23**, 439 (1912).

nucleus is $2e$ it follows that the energy at r is $4e^2/r$ or an energy much greater than that of an escaping α-particle. On classical grounds, therefore, an α-particle within the potential energy crater could never escape, disintegration would be impossible.

From the standpoint of wave mechanics, on the contrary, there is a finite probability that a particle with an energy less than that at the crater lip can exist either inside or outside the potential energy crater. The standing waves representative of the material system are not completely annihilated at the inside crater walls; they have a certain capacity to tunnel through, the probability of occurrence of the particle outside the wall being given by the square of the amplitude $|\psi|^2$ of the standing waves. The frequency of penetration of the walls is given by the same quantity $|\psi|^2$ and this must clearly diminish
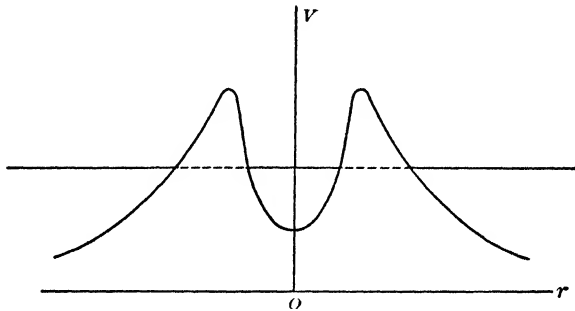
Fig. 7. Potential Crater of Disintegrating Nucleus

rapidly with increasing thickness of the wall. That is to say swift, energy-rich, α-particles will penetrate the walls more frequently, due to the shorter tunnel at the higher energy level, than the slower α-particles where the tunnel is long. This, however, is qualitatively the Geiger-Nuttall relation. The theory was tested quantitatively in two ways. Gurney and Condon defined the potential energy curve in terms of the radius at the lip of the crater and the energy at that point by use of the data of RaA ($t_{0.5} = 3.05$ mins.) as the α-emitter. Using the same values for radius and energy it was then found that the relationship employed gave the correct half-period for the observed energies of the α-particles emitted by uranium and RaC′ which have half-lives of 6.3×10^9 years and $\sim 10^{-6}$ seconds respectively. Gamow computed, for 23 α-particle emitters, the value of r at the crater lip from the known half-lives and energies of the several species. Concordant values ranging from 5.7×10^{-13} to 8.9×10^{-13} cm. were found. It is the constancy of this radius which leads to the constant values of A and B in the Geiger-Nuttall relation.

The Gamow-Gurney-Condon theory had a most important consequence in the subsequent history of nuclear physics, since it suggested to Gamow that it might not be necessary to produce nuclear projectiles with energies sufficient to reach the potential energy of the crater lip; that, on the contrary, projectiles

with lower energies than the maximum might penetrate into the crater by tunneling. It was this possibility which led Gamow to encourage trial by Cockcroft of disintegration experiments with protons of speeds moderate in comparison with those of α-particles in the Rutherford transmutation experiments. As recorded later, these trials were successful and the work on transmutation of the elements entered upon a new era of intensive development.

(31) **The Radioactive Series:** The spontaneously radioactive elements, some forty in number, with atomic weights lying, with the exception of the feebly radioactive elements K, Rb and Sm, between the atomic weight limits of 206 and 238, belong to three radioactive series. These are designated by the parent elements of each series, respectively uranium, thorium and actinium. Radium belongs to the uranium series; the parent in the actinium series is probably a uranium isotope present in constant amount in the uranium minerals. Each series, in addition to the normal sequence of disintegration products, shows a branching of the series. Thus, the change from uranium X_1 to uranium II occurs in two branches, 99.65 per cent over uranium X_2 and the residue by uranium Z; also the change from radium C to D occurs 99.97 per cent via RaC′ and 0.03 per cent via RaC″. A similar branching occurs in the thorium series from ThC to ThD, 65 per cent over ThC′ and 35 per cent over ThC″. For the actinium series a branching from AcC to AcD occurs 0.16 per cent over AcC′ and 99.84 per cent over AcC″. This branching is shown graphically for the RaC–RaD transition in Fig. 8. The UZ transition to UII is not shown on
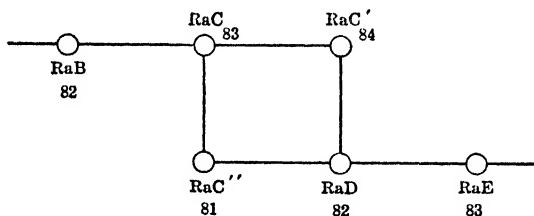
Fig. 8.   RaC–RaD Branched Transition

this diagram. The individual radioactive elements, their atomic weights and atomic numbers, together with their important constants are summarized in the three tables which follow (Tables VI, VII and VIII).

(32) **Radioactive Disintegration and the Periodic Table:** As knowledge of the properties of the elements formed in the successive stages of radioactive decay became more complete, it emerged that the loss of α-particles and β-particles by a radioactive element corresponded to a definite shift of the group classification of the elements produced in the process of decay. The loss of an α-particle in every case produced a shift, two groups to the left in the periodic table. Thus Radium (Group II) loses an α-particle to give Radon (Ra Emanation) Group 0. Similarly loss of a β-particle gives rise to a shift of one group to the right in the periodic table. The change of Radium B, Group IV,

to Radium C, Group V, is one illustration of such change. The credit for this important generalization is shared by several investigators: notably Soddy,[1] Fleck,[2] Russell[3] and Fajans.[4] Now, since the α-particle is a helium nucleus

TABLE VI

THE URANIUM SERIES

Element	Symbol	At. Wt.	At. No.	Rays	Half-life Period
Uranium-I ↓	UI	238.2	92	α	4.4×10^9 yr.
Uranium-X₁ ↓	UX₁	(234)	90	β	24.5 days
Uranium-X₂ ↓	UX₂	(234)	91	β	1.14 min.
Uranium-II ↓	UII	(234)	92	α	3.4×10^5 yr.
Ionium ↓	Io	(230)	90	α	8.3×10^4 yr.
Radium ↓	Ra	226.05	88	α	1590 yr.
Radon (Emanation) ↓	Rn	222	86	α	3.82 days
Radium-A ↓	RaA	(218)	84	α	3.05 min.
Radium-B ↓	RaB	(214)	82	β	26.8 min.
Radium-C 99.97% ⎪ 0.03%	RaC	(214)	83	β and α	19.7 min.
Radium-C′	RaC′	(214)	84	α	10^{-6} sec.
Radium-C″	RaC″	(210)	81	β	1.32 min.
Radium-D ↓	RaD	(210)	82	β	22 yr.
Radium-E ↓	RaE	(210)	83	β	5.0 days
Radium-F (Polonium) ↓	RaF	(210)	84	α	140 days
Radium-G (Uranium lead)	RaG	206	82	—	—

carrying a double positive charge and since the β-particle is none other than an electron, and since, moreover, these particles are certainly ejected from the

[1] Soddy, Chemistry of the Radio-Elements, Part II, p. 2, 1914; *Chem. News*, **107**, 97 (1913).
[2] Fleck, *J. Chem. Soc.*, **103**, 381, 1052 (1913).
[3] Russell, *Chem. News*, **107**, 49 (1913).
[4] Fajans, *Physik. Z.*, **14**, 49, 131, 136 (1913).

nucleus, it follows that the difference between the nuclei of successive atoms in neighboring groups of the periodic table consists in the extra unit of positive charge which the heavier nucleus possesses.   The atom itself being electrically neutral, it therefore follows that the extra-nuclear electrons must increase by one as the atomic table is ascended.   The progressive variation in the square root of the frequency of the characteristic X-radiation as discovered by Moseley is therefore paralleled by a progressive increase of net positive nuclear charge and of extra-nuclear electrons.

TABLE VII

THE ACTINIUM SERIES

Element	Symbol	At. Wt.	At. No.	Rays	Half-life Period
Protoactinium	Pa	(231)	91	α	3.2×10^4 yr.
↓					
Actinium	Ac	(227)	89	β	13 yr.
↓					
Radioactinium	RaAc	(227)	90	α	18.9 days
↓					
Actinium-X	AcX	(223)	88	α	11.2 days
↓					
Actinon (Emanation)	An	(219)	86	α	3.92 sec.
↓					
Actinium-A	AcA	(215)	84	α	2×10^{-3} sec.
↓					
Actinium-B	AcB	(211)	82	β	36 min.
↓					
Actinium-C 99.84% | 0.16%	AcC	(211)	83	α and β	2.16 min.
Actin.-C'	AcC'	(211)	84	α	5×10^{-3} sec.
Actin.-C''	AcC''	(207)	81	β	4.76 min.
Actinium-D	AcD	(207)	82	—	—

(33) **The Atomic Number and Defects in the Periodic Table:** It was shown that, on the basis of weight classification, certain definite transpositions of the elements would occur which would not be in harmony with the periodicity of properties shown by the bulk of the elements when arranged on a weight basis. The transposition of argon and potassium, of tellurium and iodine and of cobalt and nickel was noted.   When studied by the Moseley method, the order of the square-root of the characteristic frequencies of these elements was such as would be anticipated on the basis of properties and not that obtained on the basis of atomic weight.   Argon therefore has an atomic number of 18, potassium 19, cobalt 27, nickel 28, tellurium 52, iodine 53.   The answer to the query

of Ramsay as to the lack of complete concordance in the periodic classification was evident and revolutionary. The atomic weight is not the fundamental factor in atomic behavior. The properties of the elements are a function of their atomic architecture. Atomic weight is a secondary factor useful as a guide in the great majority of cases but at fault in the cases just mentioned and certain others now to be discussed.

TABLE VIII

THORIUM SERIES

Element	Symbol	At. Wt.	At. No.	Rays	Half-life Period
Thorium	Th	232.12	90	α	1.34 $\times$ 10^{10} yr.
Mesothorium 1	MsTh$_1$	(228)	88	β	6.7 yr.
Mesothorium 2	MsTh$_2$	(228)	89	β	6.13 hr.
Radiothorium	RaTh	(228)	90	α	1.90 yr.
Thorium-X	ThX	(224)	88	α	3.64 days
Thoron (Emanation)	Tn	(220)	86	α	54.5 sec.
Thorium-A	ThA	(216)	84	α	0.14 sec.
Thorium-B	ThB	(212)	82	β	10.6 hr.
Thorium-C	ThC	(212)	83	β and α	60.5 min.
Thorium-C'	ThC'	(212)	84	α	$c.$ 10^{-11} sec.
Thorium-C''	ThC''	(208)	81	β	3.1 min.
Thorium-D	ThD	208	82	—	—

(34) **Isotopes:** The existence of elements differing in mass yet identical in chemical properties was made familiar by the study of radioactive decay. It gradually emerged that the end product in the decay of radium was Radium G, radio-lead, identical in chemical properties with that of ordinary lead. Moreover, as the change in group classification brought about by loss of α- and β-particles became understood, it was further evident that RadiumB, Radium D and Radium G were all members of Group IV in the periodic classification. This is evident from the accompanying chart, Fig. 9. Furthermore, since loss of an α-particle (helium nucleus) results in a diminution in the atomic weight by four units, while the β-particle change is without influence on the weight,

it is evident that, by calculation of the α-particles lost in the successive changes, the atomic weights of successive products could be deduced from that of radium. Assuming an atomic weight of 226 for radium, that of RaB becomes 214
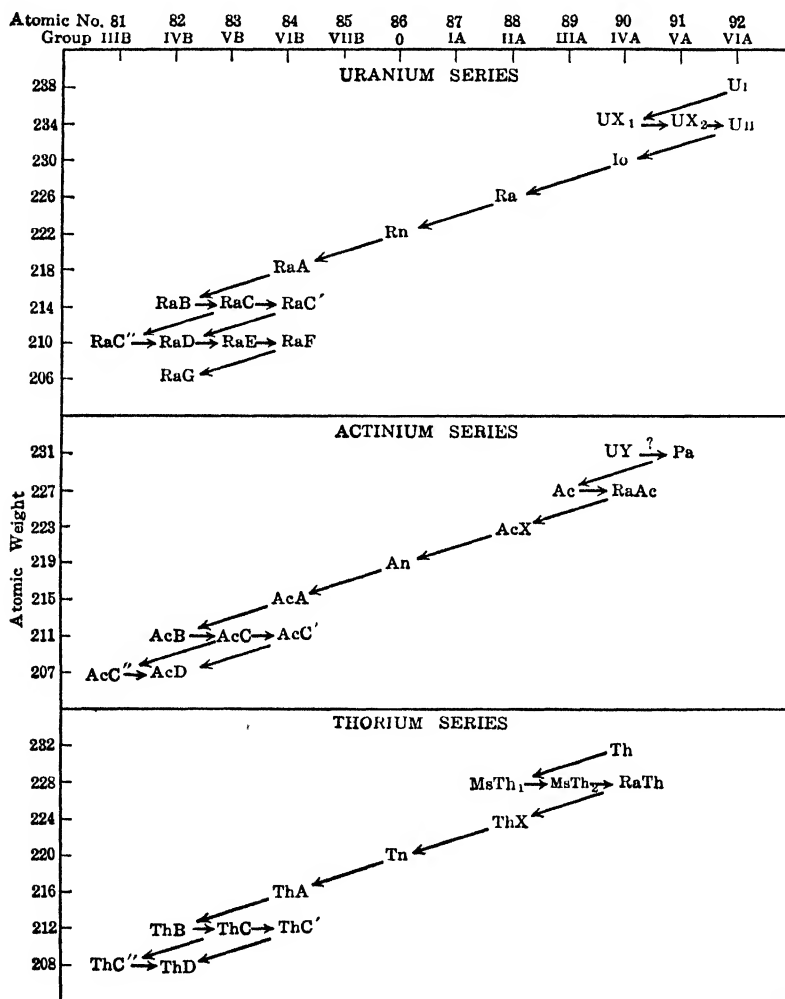

FIG. 9.   Radioactive Disintegration Series

(3 α-particles lost), that of RaD becomes 210 (4 α-particles lost), and RaG becomes 206 (5 α-particles lost). All these elements have properties identical with those of ordinary lead, whose atomic weight is 207.2, in all properties except those dependent upon mass. The masses differ as can be seen from the

above examples by so much as eight units (206–214). The end-product of the thorium series of radioactive elements is likewise a member of Group IV analogous to lead with an atomic weight of 208.1. To such elements, identical in properties other than those dependent upon mass, the term isotopes was applied. The conclusions reached upon the basis of calculation from the atomic weight of lead and the α-particle loss have been abundantly confirmed by actual atomic weight determinations.[1, 2, 3]

The wide variety of elements produced in radioactive decay, their similarity of properties, in spite of wide differences in atomic weight, would have presented a problem of considerable complexity for periodic classification had not the Moseley discovery elucidated the true basis of classification and demonstrated the secondary importance of the weight relationship. All such isotopes while differing greatly in mass are identical in atomic number. Their net nuclear charges are identical. They have a common extra-nuclear electronic configuration, and they differ only in the mass of the nucleus.

(35) **Non-Radioactive Isotopes:** The existence of atoms of identical nuclear charge but differing masses, outside the range of radioactive materials, was demonstrated by the investigations of J. J. Thomson and of Aston on the properties of the positive rays from a discharge tube. In the earlier sections, a considerable discussion has been given of the electrons liberated from atoms by the action of various forms of energy. Little has been stated concerning the residues from such changes. Positive rays were discovered by Goldstein in 1886 in the discharge of electricity through gases at low pressure. Using a perforated cathode he showed that streamers of light were present behind the cathode perforations, and assumed that the light indicated the presence of rays travelling in the opposite direction from the cathode rays. From the manner of their production he termed them 'kanalstrahlen.' Wien[4] showed that they could be deflected by a magnetic field. The detailed investigation of their properties was undertaken by J. J. Thomson,[5] who gave to them the term Positive Rays since they were shown to carry a positive charge. The rays are produced by ionization of gases at low pressures in a strong electric field of the order of 30,000–50,000 volts. They are the residues from such ionization processes.

The method of measurement employed by Thomson to investigate the charge and mass of such rays is known as the 'parabola' method. It consisted essentially in allowing the rays to pass through a very narrow tube and then in analyzing the fine beam so produced by electric and magnetic fields. Under the combined influence of an electrostatic and an electromagnetic field a ray will be deflected from its normal path and will strike a receiving screen at a point x, y, where y/x is a measure of its velocity and y^2/x is a measure of e/m,

[1] Richards and Lembert, *J. Am. Chem. Soc.*, **36**, 1329 (1914); **38**, 2613 (1916).

[2] Soddy, *J. Chem. Soc.*, **105**, 1402 (1914).

[3] Hönigschmid, *Compt. rend.*, **158**, 1796 (1914).

[4] Wien, *Verh. d. Phys. Ges.*, **17** (1898).

[5] J. J. Thomson, Rays of Positive Electricity, 1913.

the ratio of charge to mass. This follows from the application of simple dynamics to the separate actions of the electrostatic field X and the electromagnetic field H since

$$x = k \left(\frac{Xe}{mv^2} \right)$$

and

$$y = k' \left(\frac{He}{mv} \right)$$

in the manner previously demonstrated for the electron. The velocity v of the rays may vary however over a considerable range. Hence, for constant m but variable v, the locus of impact of the rays with the screen will be a parabola, pp' (Fig. 10). Rays of larger mass m' yield a similar parabola of smaller magnetic displacement qq'. The displacement of the parabolas along the magnetic axis OY at a given value along the electric field gives a measure of the relative masses since

$$\frac{m'}{m} = \frac{(pn)^2}{(qn)^2} .$$

With one known parabola, the mass of all other rays can be identified.

The sharpness of the parabolas, obtained photographically in this way by using a photographic plate as receiving screen for the rays, established experimentally for the first time the fundamental assumption of the Daltonian atomic theory, that the atoms (in these experiments the positive rays) of the same element had the same mass.

Aston improved the technique of positive ray analysis by the use of the mass spectrograph illustrated in Fig. 11. Positive rays are sorted out into a

FIG. 10.   J. J. Thomson's Parabola Method
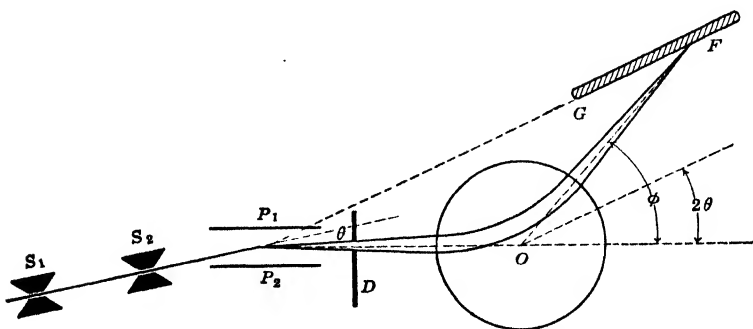
FIG. 11.   Aston's Positive Ray Spectrograph

thin ribbon by means of two parallel slits, S_1 and S_2, and are then spread into an electric spectrum by means of the charged plates P_1 and P_2. A portion of this spectrum deflected through an angle θ is selected by the diaphragm D and passed through the circular poles of a powerful electromagnet O, the field of which is such as to bend the rays back again through an angle ϕ, more than twice as great as θ. The result of this is that rays having a constant ratio m/e will converge to a focus F. If a photographic plate is placed at GF as indicated, a spectrum dependent on mass alone is obtained.

Aston [1] has been able, by successive improvements in his apparatus, to increase the accuracy of his measurements to as much as 1 part in 10,000. The early results showed that the light elements as well as the radio-elements may exist as isotopes and that the large deviations in the atomic weights of the elements from whole numbers were due to the presence of several isotopes of such masses and in such proportions as would yield the observed atomic weight.

Aston termed this observation the 'whole number rule.' This discovery removes at once the only serious objection to the unitary theory of matter which, as has been previously recorded, lay in the deviations from whole numbers in the atomic weight tables. Thus, the hypothesis of Prout was hardly tenable while exact atomic weight determinations showed the atomic weight of chlorine to be 35.457. Aston's determinations reveal chlorine as a mixture of isotopic elements of masses 35 and 37 present in such a ratio as to give an atomic weight of the mixture equal to 35.457. This is equally true of the other elements deviating from the whole number rule demanded on the basis of a unitary theory.

The discovery of isotopes explains also the remaining defect of the periodic classification, the inversion of argon and potassium, of tellurium and iodine and of cobalt and nickel in the arrangement of elements by weight. Thus, argon with an atomic weight 39.944 has isotopes of weight 40 and 36, the former in predominating amount. Potassium has two isotopes, 39 and 41, the former also largely predominating. In nuclear charge the argon isotopes are one less than those of potassium, as the Moseley investigations reveal. The relative amounts of the two isotopes in each case determine the inversion of atomic weights. The same holds true for the heavier elements tellurium and iodine, cobalt and nickel.

A second method of positive ray analysis devised by Dempster [2] causes the charged particles to fall through a definite potential difference. A narrow bundle is separated out by a slit and is bent into a semicircle by a strong magnetic field; the rays then pass through a second slit and fall on a plate connected to an electrometer. The potential difference P, the magnetic field H and the radius of curvature r determine the ratio of the charge to the mass of the

[1] Aston, *Proc. Roy. Soc.*, [A], 115, 487 (1927).

[2] Dempster, *Phys. Rev.*, 11, 316 (1918).

particle since

$$\frac{e}{m} = \frac{2P}{H^2 r^2}.$$

This method is essentially that used by Classen [1] for the determination of e/m for electrons.   Modifications of this method have been used by W. Bleakney, A. O. Nier and others for precision determinations of mass ratios in isotopic mixtures.

Dempster [2] afterwards modified his apparatus to analyze the vapors of the metals, the vapor being ionized by bombardment with electrons accelerated
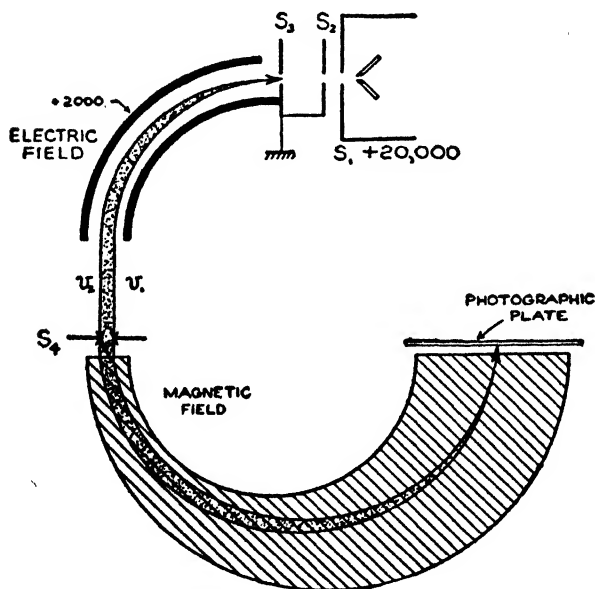

from a coated platinum strip as electron source. More recently he has developed methods using ions of elements from high frequency oscillating spark sources. A narrow ribbon of rays is selected by slit S_3, Fig. 12. The cylindrical condenser deflects them through a right angle and brings a divergent bundle of one velocity v_1 to a focus at S_4. A bundle of slightly greater velocity v_2 is reunited alongside those of velocity v_1. By making the radius of curvature in the electric

FIG 12.   Dempster's Mass Spectrograph

field the proper ratio to the radius in the magnetic field the bundles of varying energy will all reunite on the photographic plate.

The development of precision mass spectrographic methods revealed that the whole number rule was only approximate and not exact.   Deviations from integers, both positive and negative, amounting to parts per thousand of an atomic weight unit rapidly revealed themselves and became increasingly significant in the isotope field.   This significance, which will later be discussed, led to the improvements embodied by Aston in his second mass spectrograph for obtaining accurate values of atomic masses.   Improved focusing schemes were devised, culminating in the mass spectrograph of Bainbridge and Jordan [3]

[1] Classen, *Jahr. Hamburg. Wiss. Anst.*, Beiheft (1907).

[2] Dempster, *Phys. Rev.*, **20**, 631 (1922).

[3] K. T. Bainbridge and E. B. Jordan, *Phys. Rev.*, **50**, 282 (1936).

which has been very successful in obtaining the desired accuracy. Their instrument shown in Fig. 13 involves a radial electric field velocity analyzer and the magnetic focusing of ions differing in velocity. A radial electrostatic field of $\pi/\sqrt{2}$ radians, due to A. L. Hughes and V. Rojansky,[1] and a magnetic field deflecting the ions through 60° are used. The two fields are so disposed that the dispersion of ions in the electric field is exactly compensated by the dispersion of the magnetic field for a given velocity difference. This permits use of a beam of ions so divergent that higher intensities of ion beams can be successfully brought to focus.
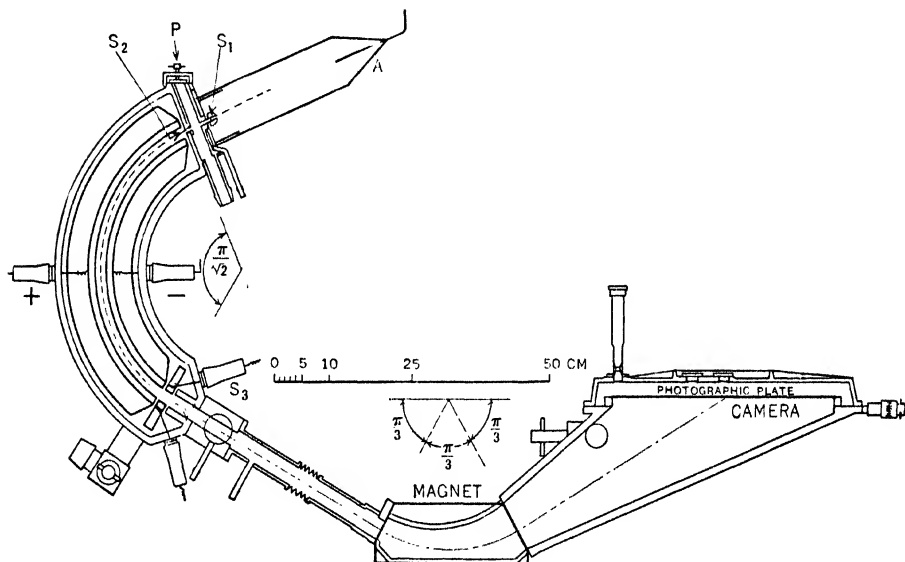
Fig. 13. Scale Diagram of Mass Spectrograph (Bainbridge and Jordan)

The ions are produced in a low pressure discharge tube at 20,000 volts. Ions of gaseous elements are obtained from the gases introduced directly into the discharge tube. Metal ions are obtained from the metal or halide salt introduced to the cathode, a discharge being operated in neon which serves to stabilize the discharge and to produce a controlled evaporation of the substance under study. The ions with energies of 15,000 to 20,000 volts are deflected through the electrostatic analyzer (radius = 25 cm.) by fields of the order of 1200 volts per cm. The plate separation of 1.9 cm. permits ions differing in energy by 4 per cent and diverging in an angle of $\frac{1}{50}$ to be focused after deflection through the $\pi/\sqrt{2}$ radians. The magnetic field operates across a 0.32 cm. gap and the pole edges are adjusted to correct for stray fields. The focusing principle thus attained has the great advantage that the mass scale along the

[1] A. L. Hughes and V. Rojansky, *Phys. Rev.*, **34**, 284 (1929).

photographic plate is *linear*, with divergencies from linearity of the order of 1 part in 7000 over a region of 14 cm.   The resolving power attained shows a value of $M/\Delta M$ = ca. 10,000 in routine work.   Coupled with these two advantages is the high collecting power, by reason of the focusing employed.

'Double focus' mass spectrographs of the types developed by Aston, Dempster, Mattauch and Bainbridge and Jordan suffer from the limitation that the focusing obtained is not completely perfect and is limited to a small range of initial velocity and direction.   A mass spectrograph designated by Bleakney [1] makes use of crossed electric and magnetic fields which permits perfect focusing properties; the focusing depends only on the m/e of the ion selected and not on the velocity or direction of the charged particles entering the analyzer.   In using this instrument, especially for the determination of abundance ratios of ions it was found that a distribution in energy amounting to 50 per cent of the accelerating potential had no effect on the resolution.

A mass spectrograph constructed by Nier which has proved to be effective in operation, and readily constructed at only moderate expense is shown in its most recent improved form in Fig. 14(a) and (b).[2]   The ionization of the gas or vapor is produced by a low voltage discharge maintained by electrons of a constant speed emitted by a heated tungsten filament T.   The electron emission is controlled by measuring the portion of the electrons passing through the slits S_1 and S_2 and reaching the Faraday cage E.   An electric field between B and C draws downward the ions formed.   The ions passing through slit S_3 are further accelerated by a large difference of potential (about 10^3 volts/cm. in routine analysis), the ion beam emerging through slit S_4.   The pair of electrodes J_1 and J_2 may be used for a finer adjustment of the ion focusing.

The ion beam enters perpendicularly the homogeneous magnetic field between the V-shaped poles of the magnet M; it is bent through such an angle as will cause the beam to leave the field boundary perpendicularly, to reach the collector through slit S_5.   The ion source (entrance slit S_4), the apex of the effective pole faces of the magnet and the collector (exit slit S_5) have to be in one straight line.

The radius of curvature of an ion in the field is given by the formula $m/e = 4.82 \times 10^{-5} r^2 H^2 / V$ where m/e is the mass-charge ratio of the ion, r the radius in cm., H the field in gauss and V the energy of the ion in electron volts. The various masses are focused by keeping H constant with varying V.   Suitable amplification and measurement of the ions collected permits a determination of relative ion peaks and hence the abundance ratios.

(36) **Precision Masses of the Ions:** The masses of the ions as determined from traces on a photographic plate are compared with that of the oxygen isotope ^{16}O.   Such a scale of masses is known as the 'physical scale' since the atomic weight tables of the chemist are constructed on the basis of O = 16, where the oxygen is now known to contain isotopes of masses 16, 17 and 18.

---

[1] W. Bleakney and J. A. Hipple, Jr., *Phys. Rev.*, **53**, 521 (1938).

[2] The details of the original form of this instrument are to be found in A. O. Nier, *Rev. Sci. Inst.*, **11**, 212 (1940).

The present accepted relation between the two scales taking account of the isotope content of molecular oxygen ($^{16}O : ^{18}O : ^{17}O = 510 \pm 40 : 1 : 0.2$) is:

Ratio of physical to chemical scale, $r = 1.00027 \pm 0.00002$.

The errors introduced into mass spectrographic measurements of mass by non-linearity of the scale or by errors of experiment have now been considerably minimized by a measurement in which ion 'doublets' having essentially the same e/m but differing in nature are simultaneously analyzed. In this way
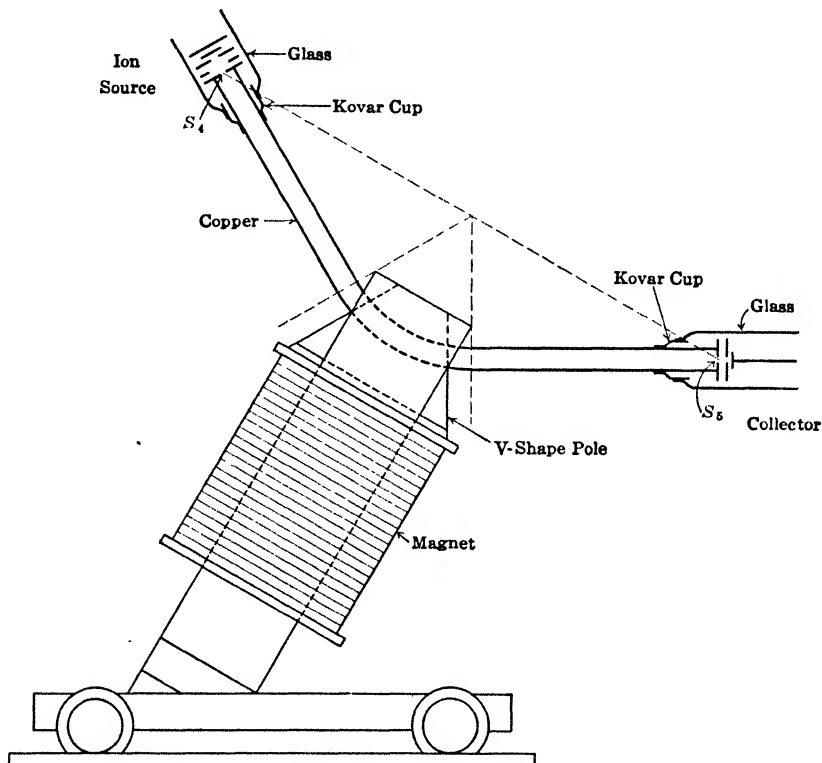
FIG. 14(a). General View, Nier Mass Spectrograph

two closely-spaced photographic traces can be obtained whose spacing represents the mass difference of the two ions. In this way the result obtained is also relatively free from errors in the calibration of the mass-scale. To illustrate the use of the method we shall consider the recent determinations by Bainbridge and Jordan [1] involving the isotopes of hydrogen, helium, lithium, beryllium, boron, carbon, nitrogen, oxygen, neon and argon.

[1] K. T. Bainbridge and E. B. Jordan, *Phys. Rev.*, **49**, 883 (1936); **50**, 98 (1936); **51**, 384, 385 (1937).

The doublets $^{12}CH_4 - {}^{16}O$, $H_2 - D$ and $D_3^+ - C^{++}$ yield the masses of H, D and ^{12}C. The helium mass comes from the separation of D_2 and He. A link between the lighter and heavier elements of the first series in the periodic table is provided by $^7Li^+$ and $^{14}N^{++}$. Carbon and nitrogen mass values were checked from the mass spectrographic data on $CO - N_2$; $CH_4 - NH_2$; $OH - NH_3$; $O - NH_2$. Especial effort was made to obtain doublets matched in intensity on the linear section of the recording plate. For beryllium, boron, neon and argon the following doublet pairs were studied $^{16}OD_2^+ - {}^{20}Ne^+$;
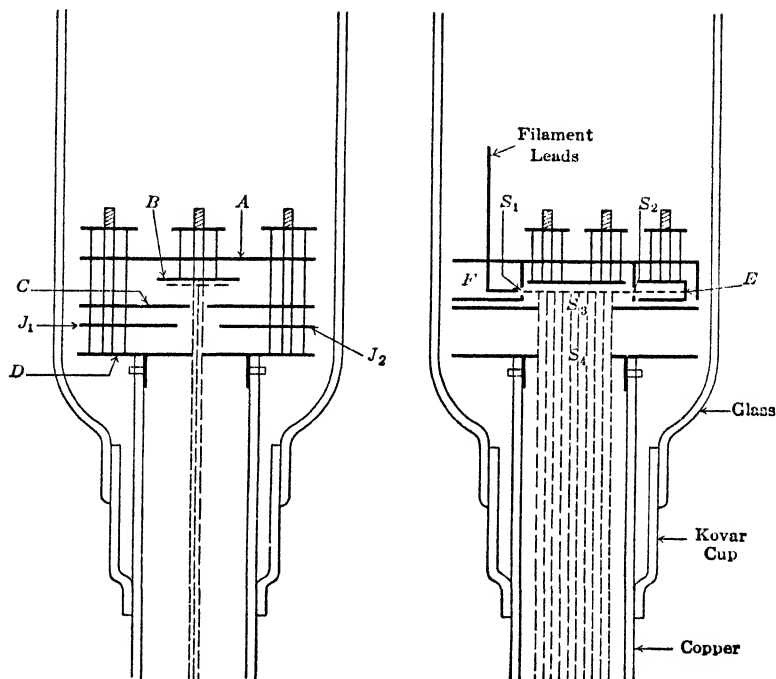
FIG. 14(b). Details of Ion Source and Slit System, Nier Mass Spectragraph

$^{10}B^+ - {}^{20}Ne^{++}$; $^{10}BH_2^+ - {}^{12}C^+$; $^{10}BH^+ - {}^{11}B^+$; $^{11}BH^+ - {}^{12}C^+$; $^9BeH - {}^{20}Ne^{++}$; $^9BeH^+ - {}^{10}B^+$; $^{11}B^+ - {}^{22}Ne^{++}$; $^{10}BH^+ - {}^{22}Ne^{++}$; $^{20}NeH^+ - {}^{21}Ne^+$; $OD_2^+ - {}^{40}A^{++}$; $^{20}Ne^+ - {}^{40}A^{++}$. Complete cycles of interlocking doublets are thereby secured giving accurate masses for most of the light elements and their isotopes. The errors involved are in general smaller than those of mass values calculated from disintegration data (see Section 49). Aston's [1] measurements in the same field agree in general with those of Bainbridge and Jordan within the experimental errors given. They extend to higher masses including ^{19}F, ^{28}Si, ^{29}Si,

[1] F. W. Aston, *Nature*, **135**, 541 (1935); **137**, 357, 613 (1936); **138**, 1094 (1936); **139**, 922 (1937); Mass Spectra and Isotopes, E. Arnold, London, 1933.

^{31}P, ^{32}S, ^{35}Cl and ^{37}Cl. The data have been examined critically by Livingston and Bethe [1] and correlated with the data accruing from disintegration data to secure 'best' values. For masses lighter than oxygen, Livingston and Bethe select the three doublets

$$H_2 - D = 1.53 \pm 0.04$$
$$D_3 - \tfrac{1}{2}{}^{12}C = 42.19 \pm 0.05$$
$${}^{12}CH_4 - {}^{16}O = 36.49 \pm 0.08.$$

The values are expressed in thousandths of a mass unit. These yield for the atomic weights in question H $= 1.00813 \pm 0.000017$; D $= 2.01473 \pm 0.000019$; ^{12}C $= 12.00398 \pm 0.00009$. From these standards the determination of other masses from ion doublets is straightforward. Table IX lists the atomic masses thus compiled by these authors, the Aston masses being included for comparison.

TABLE IX

NUCLEAR MASSES FROM MASS SPECTROGRAPH (LIVINGSTON AND BETHE)

Nucleus	Mass	Author	Aston Mass
^{1}H	$1.00813 \pm 0.0_117$	B	$1.00812 \pm 0.0_44$
^{2}H	$2.01473 \pm 0.0_42$	B	$2.01471 \pm 0.0_47$
^{4}He	$4.00389 \pm 0.0_47$	B+A	$4.00391 \pm 0.0_416$
^{7}Li	$7.01818 \pm 0.0_312$	B	
^{9}Be	$9.01516 \pm 0.0_32$	B	
^{10}Be	$10.01631 \pm 0.0_32$	B	$10.0161 \pm 0.0_33$
^{11}Be	$11.01292 \pm 0.0_316$	B	
^{12}C	$12.00398 \pm 0.0_49$	B	$12.00355 \pm 0.0_315$
^{13}C	$13.00761 \pm 0.0_315$	B	
^{14}N	$14.00750 \pm 0.0_48$	B	$14.0073 \pm 0.0_35$
^{15}N	$15.00489 \pm 0.0_32$	B	
^{16}O	16.00000		
^{18}O	$18.00369 \pm 0.0_32$	M	$18.0057 \pm 0.0_32$
^{19}F	$19.00452 \pm 0.0_33$	A	$19.0045 \pm 0.0_36$
^{20}Ne	$19.99881 \pm 0.0_311$	B	$19.9986 \pm 0.0_36$
^{21}Ne	$20.99968 \pm 0.0_323$	B	
^{22}Ne	$21.99864 \pm 0.0_336$	B	
^{28}Si	$27.9868 \pm 0.0_36$	A	$27.9863 \pm 0.0_38$
^{29}Si	$28.9866 \pm 0.0_37$	A	$28.9864 \pm 0.0_38$
^{31}P	$30.9841 \pm 0.0_35$	A	$30.9836 \pm 0.0_36$
^{32}S	$31.9823 \pm 0.0_33$	A	$31.9823 \pm 0.0_33$
^{35}Cl	$34.9813 \pm 0.0_37$	A	$34.9800 \pm 0.0_38$
^{37}Cl	$36.9788 \pm 0.0_38$	A	$36.9775 \pm 0.0_38$
^{36}A			$35.9780 \pm 0.0_21$
^{40}A	$39.97504 \pm 0.0_326$		$39.9754 \pm 0.0_214$

A = Aston.
B = Bainbridge and Jordan.
M = Mattauch.

[1] M. S. Livingston and H. A. Bethe, *Rev. Mod. Phys.*, **9**, 366 (1937).

Mattauch has re-examined the standard reference masses [1] in the light of discussions by Aston and comes to the following values:

$$^1H = 1.008130 \pm 0.0_533$$
$$^2D = 2.014722 \pm 0.0_564$$
$$^{12}C = 12.003861 \pm 0.0_424$$
$$^{14}N = 14.00753 \pm 0.0_432.$$

(37) **The Separation of Isotopes:** When the concept of isotopes was first discussed by Soddy in connection with the radioactive elements the emphasis was placed upon their chemical identity in spite of their differences in radio-active properties and atomic weights. The identity extended to spectra of the radio-elements as examined by the earlier investigators of the radio-isotopes, although, as we have seen in the preceding sections, there are limitations to this identity dependent, as we now know, on the nuclear masses. The development of the concept of the nuclear atom with the mass variable but with an identity of nuclear charge among isotopes led to an association of the identity of charge with that of chemical properties and spectra.

The examination of the lighter elements, notably neon, by the 'parabola' method and more particularly by the mass spectrograph at once revealed that, in principle at least, isotopic species were separable. The development and refining of focusing methods in mass spectrography indicated that this separation could be complete if, at the same time, minute in yield. The method demonstrated however that, in principle, any property dependent on mass could be utilized for separation without, however, assessing the attainable efficiency. Aston first tried distillation and diffusion on the neon isotopes with results, in 1913, indicative of a partial separation. Harkins tried diffusion on hydrogen chloride in 1916 and indicated in 1921 a change of 0.055 of an atomic weight unit. Other methods, discussed below, were tried in the intervening years but it was not until the spectacular success attained in the separation of the hydrogen isotopes by electrolysis in 1932–3 that significant success in isotope separation with other elements was attained. The important tool which the separated isotopes were shown to be when the hydrogen isotopes were made accessible in chemistry, physics and biology supplied the necessary spur for recent efforts in this field. We shall summarize here the methods which have been employed and the success which has been achieved, reserving to the later sections of the book, each at its appropriate place, a detailed discussion of the underlying principles. The material to be presented is based on a useful summary of this field of work recorded by Walker.[2]

The extent of separation of a mixture of two isotopic elements or compounds can be expressed quantitatively in terms of a separation or fractionation factor. If n_1 and n_2 are the numbers (or moles) of light and heavy isotopic species in a mixture before and N_1 and N_2 are the corresponding quantities after a given

[1] J. Mattauch, *Phys. Rev.*, **57**, 1155 (1940).

[2] O. J. Walker, *Ann. Rep. Chem. Soc.*, **35**, 134 (1938).

separation process which has enriched the lighter isotope then the separation factor for the lighter isotopic substance is

$$\alpha = (N_1/N_2)/(n_1/n_2). \tag{37.1}$$

If the total process be composite of a series of x single separation processes then the total or overall enrichment factor A is given by the expression $A = \alpha^x$.

(38) **Separation by the Mass Spectrograph**: The separation is as efficient as the focusing equipment of the spectrograph but the quantity separable is limited by the fact that the ion beam is small, generally of the order of 10^{-8} amp. or less. The use of crossed electric and magnetic fields for the focusing device permits the use of more divergent beams with consequent increase in ion intensities. A mass spectrograph with such fields was used to separate ^{6}Li and ^{7}Li in quantities of about 10^{-8} g.,[1] with ion currents of several hundred micro-amperes. The efficiency of separation was checked by disintegration experiments with the separate isotopes using protons and deuterons. Similar separations yielding up to 18 μg. of ^{6}Li and 200 μg. of ^{7}Li have been effected by American workers.[2, 3] The isotopes of potassium were also separated and activity measurements showed that it was the ^{41}K constituent which is radioactive, while with rubidium it was the ^{87}Rb which is radioactive. The isotopes ^{7}Li, ^{10}B, ^{11}B and ^{12}C have each been obtained [4] by mass spectrographic separations in amounts of 2–30 μg. It is for disintegration experiments [5] that these minute but efficient separations are obviously suited. Chemically they have but slight significance.

(39) **Separation by Diffusion Processes**: The velocity of diffusion of a gas through porous material is, by Graham's Law, proportional to the square root of its molecular mass. The pores of the material must be small compared with the mean free path of the molecules. Applying an analysis of the process due to Lord Rayleigh, Aston showed that for isotopes of not too great a percentage difference in mass the enrichment r of the heavier isotope m_2 is given by the expression $r = $ (Initial volume/final volume)$^{(m_2-m_1)/(m_2+m_1)}$. For neon, with a volume ratio between 500 and 10,000, r lies between 1.3 and 1.5 which corresponds to a change in density of 0.003 to 0.005 of a unit. Actually, Aston found 0.004.

Hertz [6] in 1932 enormously increased the efficiency of the diffusion process through porous tubes by incorporating them in a series of mercury diffusion pumps which permitted the diffusion to occur continuously and automatically. The pump system was so disposed that the heavier and lighter constituents accumulated at opposite ends of the system. A 24 pump unit gave a considerable separation of the isotopes of neon. A 50 pump system gave practically

[1] M. L. Oliphant, E. S. Shire and B. M. Crowther, *Proc. Roy. Soc.*, [A], **146**, 922 (1934).

[2] W. R. Smythe, L. H. Rumbaugh and S. S. West, *Phys. Rev.*, **45**, 724 (1934).

[3] L. H Rumbaugh and L. R. Hofstad, *ibid.*, **50**, 681 (1936).

[4] W. R. Smythe and A. Hemmendinger, *ibid.*, **51**, 178, 1052 (1937).

[5] E. L. Yates, *Proc. Roy. Soc.*, [A], **168**, 148 (1938).

[6] G. Hertz, *Z. Physik*, **79**, 108 (1932).

pure ^{20}Ne and a complete separation of hydrogen and deuterium. A modified
pump system, also devised by Hertz,[1] eliminated the porous tubes and operated
the diffusion process through a section of mercury vapor as the diffusion me-
dium, through which the gases to be separated pass in a direction perpendicular
to the mercury vapor stream. Higher efficiencies of separation were attained
with this type of apparatus which has been subjected to considerable theo-
retical and practical investigation.[2] Hertz tested his new system on the neon
isotopes. The isotope ratios of the three argon isotopes were displaced to
90.89, 0.51 and 8.6 and 99.74, 0.046 and 0.23 per cent for the ^{40}A, ^{38}A and ^{36}A
isotopes respectively at the two ends of the system.[3] By replacing the gas at
the 'heavy' end with 'normal' argon every six hours, a 300 hour run yielded
500 cc. at 1 mm. pressure of ^{40}A and ^{36}A in a 1 : 1 ratio from 1 liter of normal
argon at N.T.P.[4] Nitrogen gas was enriched in ^{15}N from 1.9 per cent to 20
per cent by Krüger.[5] Using 34 Hertz pumps with porous-walled units Wool-
dridge and Jenkins increased the ^{13}C concentration of methane from 1 to 16
per cent, and ^{15}N from 0.6 to 6 per cent.[6] With a battery of 51 of the new
type Hertz pumps 300 cc. of methane at 1.8 mm. pressure containing 30 per
cent ^{13}C was obtained.[7] By attaching a reservoir containing silica gel cooled
in liquid air to the light end of this system, a large reservoir of methane could
be introduced thus into the system, increasing the yields and concentration of
^{13}C methane to over 50 per cent.[8] All such researches demonstrate the utility
of the Hertz method in separating isotopic constituents but reveal at the same
time its serious limitation, the low yields of enriched gas per unit time of
operation.

(40) **Separation by Gravitational or Centrifugal Diffusion:** The barometric
formula for the variation of pressure p, with height, Δh, over the pressure $p_{1(0)}$
at sea level is given (see Vol. II) by the expression

$$p_1 = p_{1(0)}e^{-M_1 g \Delta h/RT}, \tag{40.1}$$

where M_1 is the molecular weight of the gas. The expression may be written
in terms of the number of molecules n per cc. and becomes

$$n_1 = n_{1(0)}e^{-M_1 g \Delta h/RT}. \tag{40.2}$$

For an isotopic constituent of molecular weight M_2 in admixture with the gas

[1] G. Hertz, *ibid.*, **91**, 810 (1934).

[2] H. Barwick, *ibid.*, **100**, 166 (1936); D. MacGillavry, *Rec. trav. chim.*, **56**, 330 (1937);
Trans. Faraday Soc., **33**, 433 (1937); R. Scherr, *J. Chem. Phys.*, **6**, 251 (1938).

[3] H. Barwick and W. Schutze, *Z. Physik*, **105**, 395 (1937).

[4] H. Kopfermann and H. Krüger, *ibid.*, **105**, 389 (1937).

[5] H. Krüger, *Naturwiss.*, **26**, 445 (1938).

[6] D. E. Wooldridge and F. A. Jenkins, *Phys. Rev.*, **49**, 404, 704 (1936); D. E. Wooldridge
and W. R. Smythe, *ibid.*, **50**, 233 (1936).

[7] P. Capron, J. M. Delfosse, M. de Hemptinne and H. S. Taylor, *J. Chem. Phys.*, **6**, 656
(1938).

[8] P. Capron and M. de Hemptinne, *J. phys. Radium*, **10**, 171 (1939).

M_1, the corresponding expression is

$$n_2 = n_{2(0)}e^{-M_{20}\Delta h/RT}. \tag{40.3}$$

From these two equations it follows that the separation factor α in a mixture of two isotopes due to a difference in height Δh under the influence of gravity is given by the expression

$$\alpha = (n_1/n_2)/(n_{1(0)}/n_{2(0)}) = e^{-(M_1-M_2)g\Delta h/RT}. \tag{40.4}$$

This expression was derived by Lindemann and Aston [1] and examined in detail by Mulliken.[2] Aston calculated that, for a mass difference of 2, for example the neon isotopes, the atomic weight of neon would be 20.163 at a height of 100,000 feet and 20.12 at 200,000 feet, at a mean temperature of 220° K, whereas the normal atomic weight at sea level is 20.183.

The same principle is applicable to separation under the influence of centrifugal fields and the effective separation can be enormously enchanced by the modern high speed centrifuges equivalent to many thousand fold the gravitational attraction. In the centrifuge, the velocity of motion and the centrifugal field vary from the center to the edge of the moving mass. In the case of a gas we have, for a mixture of two isotopes at total pressure p and density ρ subjected to centrifugal action,

$$dp_1 = \frac{v^2\rho_1 dr}{r} = \rho_1\omega^2 r dr = \frac{M_1 p_1 \omega^2 r dr}{RT}, \tag{40.5}$$

where p_1 and ρ_1 refer to the partial pressure and density of the lighter isotopic constituent, v, ω and r denote respectively linear velocity, angular velocity and radial distance. An analogous equation holds for the heavier constituent. The equation takes the form

$$dp_1/p_1 = \frac{M_1\omega^2 r dr}{RT} = d \ln p_1. \tag{40.6}$$

By integration

$$\ln p_1/p_{1(0)} = \frac{M_1\omega^2(r^2 - r^2_{(0)})}{2RT} = \frac{M_1(v_1^2 - v_1^2_{(0)})}{2RT}. \tag{40.7}$$

A similar equation for the heavier constituent for $\ln p_2/p_{2(0)}$ permits a combination for $v_0 = 0$ when $r_0 = 0$ of the form

$$\alpha = \frac{p_1/p_{1(0)}}{p_2/p_{2(0)}} = e^{-(M_2-M_1)v^2/2RT}. \tag{40.8}$$

The degree of separation obviously varies with increased distance from the axis of the rotating cylinder. An important feature of the centrifugal separa-

[1] F. A. Lindemann and F. W. Aston, *Phil. Mag.*, **37**, 530 (1919).

[2] R. S. Mulliken, *J. Am. Chem. Soc.*, **44**, 1033 (1922).

tion coefficient which differentiates it from many of the other methods of separation is that, being dependent only on a mass difference, it is independent of the state of combination of the element.   Further, it is obvious that the dependence on a mass difference makes it an especially favorable possibility in the case of isotope separation with heavy elements.   For this reason it has been especially considered in recent plans to separate uranium isotopes, possibly through the hexafluoride.

Mulliken called attention to a special adaptation of the centrifugal separation method which he called evaporative centrifuging.   The gaseous isotope mixture to be centrifuged is to be admitted through a tube near the axis.   With increase of speed, more and more gas would be drawn in and compressed or condensed in the periphery.   At equilibrium, with the bulk of the gas at the periphery, the gas would be drawn off very slowly by reducing the pressure at the axis.   The effect of this procedure would be analogous to a process of irreversible evaporation, the gas drawn off from the axis corresponding to the 'instantaneous condensate' in an evaporation.   Separations several fold those obtainable by a straight cut can thus be achieved.

This method has been tested recently for the concentration of the chlorine isotopes using carbon tetrachloride as the test liquid [1] and the air-driven self-balancing vacuum type centrifuges developed by Beams.   With a rotor, 11 in. long and 3 in. inside diameter containing baffles to prevent remixing, and spinning at 1060 revolutions per second, carbon tetrachloride vapor could be withdrawn from the axis at the rate of 3.2 g. per minute without decreasing the separation factor.   A separation factor of 1.025 was obtained.   Starting with 105 cc. of carbon tetrachloride in the tubular rotor, 40 cc. of liquid product with the isotopic ratio changed by 2.5 per cent in 32.5 min., or 14 cc. of liquid with a ratio change of 5 per cent in 46 min. or 1 g. of product with the ratio changed 12.8 per cent in 52.3 min. were obtained.

The separation of bromine isotopes has also been studied with the Beams-type centrifuge.[2]   Ethyl bromide was used to illustrate the applicability of the method to heavy isotopes.   The rotor, with internal diameter of 3.5 inches was operated at 1500 r.p.s. producing a centrifugal field of 388,000 g at a peripheral speed of 400 meters per second.   Spectroscopic examination of the product indicated that ^{79}Br was enriched 11 per cent relative to ^{81}Br corresponding to a decrease in molecular weight of 0.054 unit.   The theoretical separation factor was 1.0686.

(41) **Separation by Thermal Diffusion and the Clusius Method of Thermal Diffusion and Convection:** Thermal diffusion was first suggested by the theoretical investigations of Enskog [3] and independently and later by Chapman [4]

[1] J. W. Beams and C. Skarström, *Phys. Rev.*, **56**, 266 (1939).

[2] R. F. Humphreys, *ibid.*, **56**, 684 (1939).

[3] D. Enskog, *Physik. Z.*, **12**, 538 (1911); *Z. Physik*, **2**, 538 (1911); *Ann. Physik*, **38**, 750 (1912); **3**, 629 (1929).

[4] S. Chapman, *Proc. Roy. Soc.*, [A], **93**, 1 (1917); *Phil. Trans. Roy. Soc.*, **217**, 157 (1917); *Phil. Mag.*, **34**, 146 (1917); **38**, 182 (1919).

both theoretically and experimentally. If a gas mixture [1] be exposed to a temperature gradient in a reaction vessel, a diffusion process sets in whereby the lighter constituent concentrates in the hotter zone and the heavier in the colder zone. Opposed to this separation the ordinary diffusion process occurs, tending to produce uniform distribution. A stationary state is set up in which the separation per unit time produced by the thermal gradient is equal to the re-mixing in the same time produced by ordinary diffusion.

For a mixture of two isotopes Chapman deduced a relation (see also, K. Herzfeld, Vol. II) which has been given by Mulliken [2] in the form:

$$D_t = \Delta x_2 = k \ln \frac{T'}{T} = \frac{17}{3} \cdot \frac{M_2 - M_1}{M_2 + M_1} \cdot \frac{x_1 x_2}{9.15 - 8.25 x_1 x_2} \ln \frac{T'}{T} . \quad (41.1)$$

This equation is applicable to molecules which behave like elastic spheres. Δx_2 represents the difference between the two values of x_2 in the two temperature regions T' and T, with molecules of mass M_1 and M_2 not too different in mass and in mole fractions of x_1 and x_2. For hydrogen and carbon dioxide, the experiments of Dootson indicated that the separation was only 0.3 to 0.5 that to be expected from the above equation. The separation is obviously a maximum for $x_1 = x_2$ and it can be computed from the above equation that, in such a 50 : 50 mixture of hydrogen and carbon dioxide and a gradient of temperature from 400° C. to room temperature, the maximum separation should not exceed a ratio of 56 : 44 for the two gases. Applied to most isotopic mixtures the separations attainable should be correspondingly smaller. Thermal diffusion alone should therefore be a poorer separation agent than ordinary diffusion although it offers the advantage of continuous operation. A number of researches by Ibbs and his collaborators [3] from 1921 to 1932 were concerned with the effects of temperature gradient, gas pressure and composition, measuring the separations attained by thermal conductivity. Interferometric methods of measurements were employed by G. and O. Blüh. [4]

A new principle was introduced by Clusius and Dickel [5] in that they utilized the temperature gradient necessary to produce the thermal diffusion also to bring about a thermal convection whereby the hot gas was carried in the opposite direction to the cold gas thus multiplying the effect of the separation due to thermal diffusion. In their apparatus an electrically heated vertical wire serving as the hot surface was disposed axially in a cylindrical tube the outside of which was kept cool. Between the two, the gas mixture, at a suitable pressure, was subjected to separation due to thermal diffusion and, in addition, due to the thermal siphon effect, the gas rising at the hot surface carried the

[1] S. Chapman and Dootson, *ibid.*, **33**, 248 (1917).

[2] R. S. Mulliken, *J. Am. Chem. Soc.*, **44**, 1035 (1922).

[3] T. L. Ibbs *et al.*, *Proc. Roy. Soc.*, [A], **99**, 385 (1921); **107**, 470 (1925); *Proc. Phys. Soc.*, **39**, 227 (1927); **41**, 456 (1929); **43**, 142 (1931); **44**, 613 (1932).

[4] G. and O. Blüh, *Z. Physik*, **90**, 12 (1934).

[5] K. Clusius and G. Dickel, *Naturwiss.*, **26**, 546 (1938).

lighter constituent in excess upwards, the gas falling at the cold surface similarly concentrating the heavier constituent.

In tubes of one meter length and 1 cm. diameter heated by a nichrome wire 0.3 mm. in diameter, with a temperature gradient in different experiments varying from 300 to 600° C., it was shown that bromine in helium and carbon dioxide in hydrogen could be practically completely separated. With a 3 meter tube a four-fold concentration of oxygen in air and a three-fold concentration of the heavy neon isotope were secured. In the same tube a displacement of the chlorine isotopes in hydrogen chloride from 76 : 24 to 60 : 40 was secured in one operation.

Clusius and Dickel[1] later recorded a series of five experiments in which hydrogen chloride was separated simultaneously into its constituents $H^{35}Cl$ and $H^{37}Cl$. Four tubes were employed of 8, 7, 6 and 6 meters respectively of 8.4 mm. internal diameter and a fifth tube 9 meters long and 12.8 mm. internal diameter. These five could be operated in series, gas from the bottom of one column being brought to the head of the next column in series by means of a thermally operated circulation system. Parallel operation of some of the columns was also possible. Five different dispositions of the columns were tried in the five series of experiments. The separation obtained in the final two series is best indicated by the following data.

	Light End	Heavy End
Atomic weight (theoretical)	34.971	36.968
Atomic weight (found)	34.979	36.956
Difference	0.008	0.012
Purity	99.6% ^{35}Cl	99.4% ^{37}Cl

The energy expenditure for the electric heating of the wire was 2.5 kilowatts and in 24 hours 8 cc. $H^{37}Cl$ and 25 cc. $H^{35}Cl$ were obtained.

W. Groth[2] has tested the Clusius method on the xenon isotopes in comparison with the Hertz diffusion process. A 12-stage Hertz pump system gave a displacement of 0.5 unit in the atomic weight in 12 hours at 2 mm. pressure. The same displacement can be secured at atmospheric pressure in a 2.5 meter tube 12 mm. wall diameter, heated axially by a tungsten wire at 1000° C. With a 5 mm. tube and a wire temperature of 1750° a displacement of 1.6 atomic weight units was secured.

The separation of the chlorine isotopes by Clusius and Dickel represents an experimentally favorable case since the separation factor due to thermal diffusion on the Chapman basis is proportional to the product $x_1 x_2$ which, in this case, is 0.76×0.24. The separation of the carbon isotopes is much less favorable since the abundance ratio $^{12}C : ^{13}C$ is 0.99 : 0.01. Experiments by G. G. Joris[3] using methane with 3-meter columns with hot and water-cooled glass surfaces at wall distances of 7.5 to 10 mm. and mean gas temperature of 400° K

[1] K. Clusius and G. Dickel, *Z. physik. Chem.*, **B, 44**, 397, 451 (1939).

[2] W. Groth, *Naturwiss.*, **27**, 260 (1939).

[3] H. S. Taylor, *Nature*, **144**, 8 (1939).

gave a separation factor $\alpha = 2$. A 12 meter iron tube 2 cm. internal diameter, heated axially by No. 16 chromel wire gave a separation factor of 3 with a heating current of 6 amps. and a separation factor of 20 with a heating current of 9 amps. In the latter case a ^{13}C concentration averaging 1.1 per cent was thus changed to 0.1 at the top of the column and 2 per cent at the bottom of the column. Similar efficiencies of separation have been reported with methane by Taylor and Glockler,[1] by Watson[1] and more recently by Nier.[2] The column used by Nier was 24 ft. long, the hot surface of iron with an outside diameter of 0.75 in., the water-cooled surface a cylinder of brass, 2 in., diameter. The hot temperature was approximately 300° C. and the outer wall 27° C. Power consumption was 2.75 kilowatts. At 65.6 cm. pressure the separation factor changed from 1 initially to 3.23, 3.99, 4.23, 4.06 at 9, 23.5, 46 and 73 hours. It fell again at 21.7 cm. pressure to ~ 2. Traces of carbon monoxide and carbon dioxide present as impurities in the gas concentrated at the bottom of the column, the efficiency of separation being indicated by separation factors (CO/CH_4) and (CO_2/CH_4) at the bottom and top of the column respectively 100–180 and 1000–2000. The various ratios of the constituents were determined mass spectrographically.

The factors which determine the efficiencies of such columns have been examined in detail by Clusius and Dickel, using air as the gas investigated. We may define a quantity n, the transport of gas in the column, as the number of cc. of the heavy constituent of the initial mixture brought into the column by the separating action of the thermal diffusion. Clusius and Dickel find this to be proportional to (1) the separation factor at the point of entry of fresh gas, (2) the time, (3) the square of the pressure, (4) the fourth power of the radius. Within small temperature intervals the transport is proportional to the square root of the temperature and it is also independent of the length of the column. For laminar flow, the volume of gas V entering the column per unit time is proportional to the fourth power of the radius and the force K determining the flow

$$V \propto Kr^4. \qquad (41.1)$$

The force K is proportional to the density difference between hot and cold gas and so varies linearly with the pressure, p, i.e.,

$$V \propto pr^4. \qquad (41.2)$$

Now, since the number of molecules in a given volume is proportional also to p, it follows that the transport n is proportional to pV and hence

$$n \propto p^2r^4. \qquad (41.3)$$

This is the experimental conclusion reached in (3) and (4) above.

[1] T. I. Taylor and G. Glockler, *J. Chem. Phys.*, **7**, 851 (1939); **8**, 843 (1940); W. W. Watson, *Phys. Rev.*, **56**, 703 (1939).
[2] A. Nier, *ibid.*, **57**, 30 (1940).

The concentration obtained at the bottom of a tube with a large reservoir of initial gas at the upper end is a measure of the separation efficiency of a column. Clusius and Dickel find this to be proportional to the Chapman-Enskog separation factor and inversely proportional to the fourth power of the radius and the square of the pressure. The time taken for a molecule to pass from the hot wire to the cold wall is from the diffusion equation (Vol. II)

$$\Delta t = \frac{\overline{r^2}}{2D},\tag{41.4}$$

where r is the tube radius and D the diffusion coefficient. The volume of gas rising in the tube is proportional to the fourth power of the radius (see above) and its velocity v is proportional to the square of the radius. Thus,

$$v = \frac{\Delta l}{\Delta t} = ar^2.\tag{41.5}$$

Combining these two equations

$$\Delta l = \frac{a}{2D}\, r^4.\tag{41.6}$$

The reciprocal of this length is proportional to the gradient of concentration i.e.,

$$\frac{x_e - x_i}{l} \approx \frac{dx}{dl} \propto \frac{1}{\Delta l} = \frac{2D}{ar^4} \propto r^{-4},\tag{41.7}$$

where x_e and x_i are the end and initial mole fractions of the given constituent. The convection velocity is also proportional to the pressure

$$\frac{\Delta l}{\Delta t} \propto p.\tag{41.8}$$

Also, since the diffusion coefficient varies inversely as the pressure,

$$\Delta t = \frac{\overline{r^2}}{2D} = \frac{\overline{r^2}}{2}\, p,\tag{41.9}$$

whence, by combining these two expressions, we obtain

$$\Delta l \propto \frac{\overline{r^2}}{2}\, p^2,\tag{41.10}$$

or, for the reciprocal length, proportional to the gradient of concentration.

$$\frac{x_e - x_i}{l} = \frac{dx}{dl} \propto p^{-2}.\tag{41.11}$$

These considerations assume implicitly that ordinary diffusion along the length of the column is negligible. Such diffusion will always diminish the observed separation.

The efficiency of a Clusius column can be stated in terms similar to those used in expressing the efficiency of a fractionating column generally formulated in terms of the number of theoretical plates. The Clusius column can be measured in terms of the number of *ideal separation units* of which it may be regarded as composed. An ideal unit can be measured as the length of column, Δl, through which, in the cold gas, the gradient of concentration of the heavy constituent is equal to that gradient of concentration obtaining due to thermal diffusion under constant and specified temperature conditions from hot to cold surface. A column at equilibrium may be thought of as a succession of such ideal units one above the other, whose effects are additive. For a given gas it is evident that the ideal unit has a length which is independent of gas composition, provided, of course, that at all parts of the column identical conditions of dimensions and temperature prevail.

For air, in a 93 cm. column, Clusius and Dickel found that the mole fraction of oxygen was enriched from 0.209 to 0.395 at the heavy end. The mean concentration was therefore 0.5 (0.209 + 0.395) = 0.302. For such a composition of nitrogen-oxygen mixtures the Chapman equation gives a thermal diffusion separation factor of 0.0126. Since the theoretical figure has been found generally to be too great by a factor of 2 we may assume 0.006 as the mean concentration gradient across the hot-cold gap. Since the total displacement of concentration from bottom to top of column was 0.395 − 0.209 = 0.186, the column may be thought of as equivalent to 0.186/0.006 = 31 ideal units. It is evident from such considerations how effective the Clusius-Dickel procedure is in amplifying the separation efficiency due to thermal diffusion. The ideal unit is, in this case and for this gas mixture, about 3 cm. in length.

The concentration gradient Δx can be expressed in terms of the column length Δl, the length of the ideal unit l_i and the thermal separation coefficient D_t

$$\Delta x = \frac{\Delta l}{l_i} D_t. \tag{41.12}$$

Inserting the Enskog equation for D_t and collecting all constants in K this yields the differential expression

$$dx = \frac{K}{l_i} \cdot \frac{M_2 - M_1}{M_2 + M_1} \ln \frac{T'}{T} \cdot x_2(1 - x_2), \tag{41.13}$$

from which, by integration, the length of tube required for initial concentration x_i of the heavy constituent at the top and end concentration x_e at the bottom is given by

$$l = \frac{l_i}{K} \cdot \frac{M_1 + M_2}{M_2 - M_1} \ln \frac{T}{T'} \ln \frac{x_i(1 - x_e)}{x_e(1 - x_i)} . \tag{41.14}$$

The separation factor α for the column thus becomes

$$\alpha = \frac{x_e(1 - x_i)}{x_i(1 - x_e)} = e^{lK/l_i \cdot (M_2 - M_1)/(M_2 + M_1) \cdot \ln T'/T}, \tag{41.15}$$

which, for a given gas, in a tube of constant dimensions and operating conditions, gives

$$\alpha = e^{kl}, \tag{41.16}$$

where

$$k = K(M_2 - M_1)(\ln T'/T)/l_i(M_2 + M_1).$$

Waldmann [1] has further developed the theory of the diffusion-thermal convection process and arrives at a similar expression for the overall separation factor which differs however in the term involving the temperature. Waldmann's expression gives the separation in terms of the temperature gradient ΔT and the mean temperature T_m in the following form

$$\alpha = \exp\left[\text{const.} \times (M_2 - M_1)/(M_2 + M_1) \times \Delta T^{4/3}/T_m^{5/3}\right]. \tag{41.17}$$

Furry, Jones and Onsager [2] have developed the theory of the process for an apparatus composed of two concentric tubes, one hot, one cold, as used by Brewer and Bramley.[3] Their theory has been tested recently by Nier [4] on the concentration of ^{13}C in methane with the experimental results already cited The separation factor according to this theory is again of the form $\alpha = e^{\text{const.}\, l}$, where the constant in the equation has the form

$$2A_d = 2A/(1 + K_d/K), \tag{41.18}$$

where

$$A = 252(a\eta D/\rho g d^4)f(\Delta T/T) \tag{41.19}$$

and

$$K_d/K = 1890(T_1^2 + T_1 T_2 + T_2^2)(8D\eta/d^3\rho g \Delta T)^2, \tag{41.20}$$

where η = coefficient of viscosity; D = coefficient of diffusion; ρ = density of gas; g = gravitational acceleration; d = thickness of annular gas space; T_1, T_2 = absolute temperature of outer and inner tube, $\Delta T = T_2 - T_1$; $D_t/D = aC_1C_2$ where D_t = coefficient of thermal diffusion and C_1, C_2 represent concentrations of heavy and light components of the gas mixture.

Since D varies inversely as the density ρ and the pressure also varies as the density it follows from the equations given that

$$2A_d l = (x/p^2)/[1 + (y/p^4)] = Z, \tag{41.21}$$

where x and y are constants independent of the pressure and p is the pressure in atmospheres. In the case of methane since ^{13}C is always $\lessgtr 1$ per cent we may write for $^{13}CH_4$ at top and bottom of the column

$$C_1^B/C_1^T = e^Z. \tag{41.22}$$

Nier used two sets of data to determine the constants x and y in the equation

[1] L. Waldmann, *Naturwiss.*, **27**, 230 (1932).

[2] W. H. Furry, R. C. Jones and L. Onsager, *Phys. Rev.*, **55**, 1083 (1939).

[3] A. K. Brewer and A. Bramley, *ibid.*, **55**, 590A (1939); *J. Chem. Phys.*, **7**, 553 (1939).

[4] A. Nier, *Phys. Rev.*, **57**, 30 (1940).

for Z and tested it on a third set of data with excellent agreement with theory so far as pressure is concerned. Calculation showed also that the experimental values of x and y were in reasonable agreement with the theoretical equations of Furry, Jones and Onsager and that the power consumption of 2 kw. was also in agreement with theoretical expectation. Bardeen [1] has analyzed the theory also to determine the rate of approach to equilibrium obtaining solutions for the time-dependent partial differential equation in good agreement with Nier's experimental results.

(42) **Separation by Electrolysis:** (a) *Hydrogen.* The separation of isotopes by electrolysis, suggested by Kendall and Crittenden [2] in 1923, came to fruition in the observation of Washburn and Urey [3] that samples of water from electrolytic hydrogen-oxygen cells were measurably richer in the hydrogen isotope of mass 2. Lewis and his collaborators [4] thereupon demonstrated that prolonged electrolysis could be used to isolate the pure deuterium (^{2}H or D), free from the lighter isotope.

Many techniques of producing heavy water (D_2O) by electrolysis have been described; the procedure most frequently employed subjects 0.5 molar sodium hydroxide solution to continued electrolysis, using nickel or nickel and iron electrodes, until a given solution is reduced to 10–20 per cent of its initial volume. The concentrated electrolyte so produced may be neutralized with carbon dioxide, distilled to remove the carbonate and then subjected to further electrolysis after being brought to 0.5 molar sodium hydroxide by suitable addition of undistilled concentrated electrolyte. A succession of electrolyses produces successively increasing concentrations of deuterium in the residual

TABLE X

Concentration of Deuterium by Electrolysis

Stage	Liters of Solution Electrolyzed	Density (d_4^{20})	Deuterium Content of Residue
1	2300	0.998	~0.1%
2	340	0.999	0.5
3	52	1.001	2.5
4	10	1.007	8.0
5	2	1.031	30.0
6	0.42	1.098	93.0
7	0.08	1.104	99.0

liquor as indicated in Table X for successive stages of concentration of electrolyte from commercial cells.[5] After the third stage, the hydrogen evolved during

[1] J. Bardeen, *ibid.*, **57**, 35 (1940).

[2] J. Kendall and E. D. Crittenden, *Proc. Nat. Acad. Sci.*, **9**, 75 (1923).

[3] E. W. Washburn and H. C. Urey, *ibid.*, **18**, 493 (1932).

[4] G. N. Lewis, *J. Am. Chem. Soc.*, **55**, 1297 (1933); G. N. Lewis and R. T. Macdonald, *J. Chem. Phys.*, **1**, 341 (1933); *J. Am. Chem. Soc.*, **55**, 3058 (1933).

[5] H. S. Taylor, H. Eyring and A. A. Frost, *J. Chem. Phys.*, **1**, 823 (1933).

the electrolysis contains an amount of heavy isotope sufficient to justify recovery. This is accomplished by recombining the electrolytic gas evolved and turning the water back into the system at the appropriate stage, normally the immediately preceding stage, since the normal separation factor α is approximately 5 where $\alpha = [H/D]_{gas} \div [H/D]_{liq}$. The fractionation factor in the vaporization of water, 1.025, is much smaller than that of electrolysis. Hence, to minimize losses of heavy isotope by evaporation the electrolytic cells are kept suitably cooled during electrolysis, generally with running water.

Both acid and alkaline electrolytes may be used for the electrolysis and various metals used as electrodes give different separation efficiencies. The following data from the work of Topley and Eyring [1] illustrate these factors.

TABLE XI

SEPARATION FACTORS FOR VARIOUS CONDITIONS OF ELECTROLYSIS

Electrode	Electrolyte	Separation Factor
Lead.	0.5N KOH	7.2 – 7.4
Platinum	"	6.5 – 7.6
Platinum	0.5N H$_2$SO$_4$	5.7
Iron	0.5N KOH	6.9 – 7.6
Nickel	"	5.5
Copper	"	6.8
Silver	"	5.3 – 5.8

The data refer to massive metals as electrodes, at current densities of the order of 1 amp. per sq. cm. in each case. The separation factor normally increases somewhat with increasing current density and decreases with increasing temperature. There is definite evidence pointing to a constant separation factor with varying deuterium content of electrolytic solution in the intermediate ranges but data of Applebey and Ogden [2] indicate that, with a nickel cathode and a 5 per cent sodium hydroxide solution, the separation factor passes from 5.2 at 3.7 per cent D$_2$O, to 5.56 at 29.5 per cent, to 4.35 at 58.7 per cent and 3.45 at 86.5 per cent D$_2$O. Some data of Trenner [3] indicate a low separation factor in solutions approaching pure deuterium oxide.

It is known that the exchange reaction,

$$H_2O_l + HD = HDO_l + H_2$$
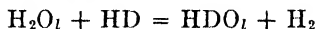
can be catalyzed at metal electrode surfaces.[4] The equilibrium constant for this reaction, which may be written in the form $K = \alpha = [H_2]/[HD] \div [H_2O]_l/[HDO]_l$ for dilute deuterium concentrations has a value of about 3 for ordinary temperatures. The operation of this equilibrium at the surface of the electrodes tends therefore to diminish the electrolytic separation factors obtained. Platinized platinum electrodes are notable for the low separation

[1] B. Topley and H. Eyring, *J. Chem. Phys.*, **2**, 217 (1934).

[2] M. P. Applebey and G. Ogden, *J. Chem. Soc.*, 163 (1936).

[3] N. R. Trenner, *J. Am. Chem. Soc.*, **59**, 1391 (1937) and unpublished measurements.

[4] A. and L. Farkas, *J. Chem. Phys.*, **2**, 468 (1934).

coefficients which they yield and are also known to catalyze the exchange reaction. At low current densities the maximum separation factor attainable would, in this case, be 3 as is approximately found.

A comprehensive investigation of the influence of the cathode material was carried out by Eucken and Bratzler,[1] special attention being paid to the previous history of the material. The results reported were erratic, separation factors for platinum between 3.4 and 14.7, for gold $3.1-17.6$, for silver $4.1-9.1$ and for lead $4.0-9.8$ being found. They concluded that there was no parallelism between the actual overvoltage and the separation factor which latter was increased by previous anodic treatment of the electrode. Poisons such as α-naphthaquinoline decreased the separation factor.

Horiuti and Okamoto [2] found that the separation factors at metal cathodes with normal sulfuric acid in 6 per cent D_2O as electrolyte were divided into two groups, from 6 to 7 with Ni, Au, Ag, Cu and Pt and a value of 3 with Sn, Hg and Pb. The result with lead is in disagreement with Topley and Eyring who found $\alpha = 7.2-7.4$ in potassium hydroxide and $6.2-6.6$ in sulfuric acid. Horiuti and Okamoto found $\alpha = 6.8$ with normal potassium hydroxide. They suggest that the two groups correspond to two different cathodic mechanisms of hydrogen evolution. The first stage is common to both, a transfer of a proton from hydrogen ion (H_3O^+) to the metal.

$$M + H^+H_2O \xrightarrow{\ +e\ } M-H + H_2O \text{ (rapid)}.$$
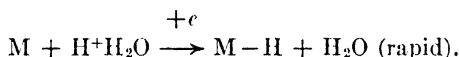
Two alternative processes follow, one of which is the rate-determining slow step:

I. A catalytic mechanism: $2M-H = 2M + H_2$.
II. An electrochemical mechanism: $M-H + H^+H_2O = M + H_2 + H_2O$.

In the latter case other proton donors might act in place of H^+H_2O. The mechanism predominating would depend on conditions: if the metal is a good catalyst or the acid concentration is small or if both simultaneously obtain, then reaction I will predominate, the separation factor approximating to 6. If the metal is a poor catalyst, the acid concentration high, or if both obtain, mechanism II will predominate. Poisoning or change of acid concentration may cause the predominant mechanism to change.

The data of Walton and Wolfenden [3] confirm the existence of two groups of metals with different separation factors, and the influence of temperature on separation is traced. Their values for α are summarized in Table XII. In the experiments with mercury, $0.5N$ HCl $+ 0.5N$ KCl was used in 30–50 per cent D_2O. The electrolyte for the other metals was 0.2 to $0.5N$ H_2SO_4 in 30–50 per cent D_2O.

[1] A. Eucken and K. Bratzler, *Z. physik. Chem.*, **174**, 279 (1935).
[2] J. Horiuti and G. Okamoto, *Sci. Papers Phys. Chem. Res. Tokyo*, **28**, 231 (1936).
[3] H. F. Walton and J. H. Wolfenden, *Trans. Faraday Soc.*, **34**, 436 (1938).

TABLE XII

INFLUENCE OF TEMPERATURE AND ELECTRODE MATERIAL ON THE
SEPARATION FACTOR

Metal	15°	20°	55°	85°	95°
Hg	3.3		3.5		3.3
Sn	3.0		3.2		4.0
Ag	6.0				4.3
Ni		7.0		5.9	
Pt		5.3		3.2	

With low separation factors the temperature coefficient is small but may be negative (Hg) or positive (Sn). With large separation factors there is a large negative temperature coefficient in each case. Increase of current density decreases α with Hg, Sn, Ag and Ni, but increases it slightly with Pt; the effect decreases with increasing temperature. Walton and Wolfenden suggest that at Ag, Ni and Pt electrodes the slow process is either catalytic ($2H \rightarrow H_2$; Horiuti and Okamoto) or proton transfer involving the Erdey-Grúz–Volmer theory of overvoltage (see Vol. III). At Hg surfaces the slow process is assumed to be electrochemical. The fact that arsenious oxide has little effect on the separation factor at Ag and Ni cathodes seems to be opposed to the catalytic mechanism. A. Farkas found that the separation factor at a palladium cathode was different for the occluded gas (6.6) and for that evolved (4.4).

Theoretical discussion of the electrolytic separation of hydrogen and deuterium has quite generally turned upon the influence of overvoltage upon the different rates of evolution of the two isotopes, and indeed on the precise mechanism of overvoltage which might be responsible. Eyring and Sherman [1] early pointed out that the formation and liberation of the molecular hydrogen isotopes at the electrode might yield a separation factor of 4 on purely kinetic considerations and that differences in zero-point energy between the Me − H and Me − D bonds would tend to raise this value. Gross and Halpern [2] and Urey and Teal [3] treated this point of view more fully and showed that it would lead to reasonable values for the separation factor.

Bell,[4] arguing from a supposed independence of the nature of the cathode material, decided in favor of Gurney's mechanism of overvoltage (Vol. III), the slowness of passage of electrons over a potential barrier, the slowness, therefore, of the reaction between H_3O^+ or H^+ with electrons to produce the atom. Urey and Teal found that reasonable values of the separation coefficient could thus be calculated. It would appear therefore that the electrolytic separation of the hydrogen isotopes would not furnish an unequivocal answer to the problem of the mechanism of overvoltage.

[1] H. Eyring and A. Sherman, *J. Chem. Phys.*, **1**, 345 (1933).
[2] P. Gross and O. Halpern, *ibid.*, **3**, 452 (1935).
[3] H. C. Urey and G. K. Teal, *Rev. Mod. Phys.*, **7**, 34 (1935).
[4] R. P. Bell, *J. Chem. Phys.*, **2**, 164 (1934).

More recently, Eyring, Glasstone and Laidler [1] have suggested a mechanism based upon the new theory of overvoltage developed by them. This theory is based upon the absolute reaction rate theory of chemical reactions (Vol. IV) and relates the current density I at an electrode to the overvoltage V by means of the expression $I = I_0 \exp (\alpha VF/RT)$ where I_0 is a constant for a given electrode representing the current passing in each direction at the reversible potential and α is the fraction of the added potential V operating between the initial state and the activated state of the system. The examination of I_0 in terms of the heat and entropy changes of the activation process suggests that the slow process may consist in the transfer of a proton from a molecule of water in the solution to another water molecule attached to the electrode surface. This prototropic mechanism is shown to be consistent with the higher overvoltage for deuterium necessary to account for the observed separation factors, and to be due to a difference of approximately 1.2 kcal. between the heats of activation of the deuterotropic and prototropic processes. The theory explains satisfactorily not only the magnitude of the separation factor and its variation with electrode material. It also accounts for the variation of the separation factor with temperature. It is with respect to these two last factors that the superiority of this newer theory of overvoltage over preceding theories is marked.

(*b*) *Other Elements:* The success which attended the separation of the hydrogen isotopes by electrolysis led to the examination of the method for other isotopes. Washburn and Urey [2] discussed the possibility of oxygen separation. Electrolysis of 117 liters of $0.5N$ sodium hydroxide with nickel anodes down to 1 cc. gave a steady increase in concentration from 0.202 to 0.222 per cent, the 10 per cent increase corresponding to a separation factor of only 1.01.[3] H. L. Johnston, using iron electrodes, fractionated potassium hydroxide solution by electrolysis, recombining the hydrogen and oxygen to form water which was again electrolyzed. The density change was rapid at first due to deuterium removal but the subsequent change in density due to ^{18}O enrichment indicated a separation factor of 1.008. Tronstad and Brun [4] reported a factor of 1.034, which should have given in the earlier experiments recorded a very marked enrichment of ^{18}O.

The separation of ^6Li from ^7Li electrolytically has been studied by T. I. Taylor and Urey,[3] by Holleck,[5] and by Johnston and Hutchison.[3] Twenty electrolyses of 800 cc. of a 10 per cent solution of lithium hydroxide with nickel anode and a rapidly stirred mercury cathode, until only 1 g. of hydroxide remained, were made, mercury being continuously run through the cell to remove the lithium amalgam formed. The residual solutions were united, concentrated

[1] H. Eyring, S. Glasstone and K. Laidler, *ibid.*, **7**, 1053 (1939).

[2] E. W. Washburn and H. C. Urey, *Proc. Nat. Acad. Sci.*, **18**, 496 (1932).

[3] P. W. Selwood, H. S. Taylor, J. A. Hipple and W. Bleakney, *J. Am. Chem. Soc.*, **57**, 642 (1935).

[4] L. Tronstad and J. Brun, *Trans. Faraday Soc.*, **34**, 766 (1938).

[5] T. I. Taylor and H. C. Urey, *J. Chem. Phys.*, **5**, 597 (1937); L. Holleck, *Z. Elektrochem.*, **44**, 411 (1938); H. L. Johnston and C. A. Hutchison, *J. Chem. Phys.*, **8**, 869 (1940).

and electrolyzed. The ratio of initial to final lithium was 600 : 1 and the isotopic ratio ^7Li : ^6Li was changed from 12.5 : 1 to 14.2 : 1 corresponding to a separation factor of 1.020. Later experiments [1] with lithium chloride gave a factor of 1.039. Johnston and Hutchison in still later experiments find 1.055 ± 0.005. Holleck's experiments with the chloride changed the atomic weight of lithium from 6.941 to 6.894, corresponding to an enrichment of ^6Li by 71 per cent of the concentration originally present. Lewis and Macdonald [2] displaced the atomic weight to 6.855 by exchanging lithium amalgam with lithium salt solutions (chloride in alcohol; bromide in alcohol-dioxane). The amalgam is preferentially enriched in ^6Li. The atomic weight of 6.855 corresponds to an increase in the ratio ^6Li : ^7Li from 1 : 11.6 to 1 : 5.1. The method depends on the difference in electrode potentials of the two isotopes.

(43) **Separation by Fractional Distillation:** Aston did not achieve any measurable separation of neon isotopes by fractional distillation from charcoal cooled in liquid air. Keesom and van Dijk, by rectification of neon in the neighborhood of its triple point have produced fractions with atomic weights of 20.091 and 20.574 from the normal neon of atomic weight 20.183.[3] Similarly, by rectification, Smith [4] has obtained a sample of atomic weight 21.157. Urey and his collaborators [5] obtained their first indications of deuterium through distillation of liquid hydrogen. Small increases in the concentration of ^{18}O have been secured by distillation of liquid oxygen.[6] Only a slight concentration of ^{15}N was obtained by distillation of ammonia.[7]

The fractional distillation of water was shown by Lewis and Cornish [8] to produce small changes in density and to this change the disturbance of the oxygen isotope ratio was also a contributing factor. Urey and Wahl [9] found that the separation factor for the oxygen isotopes in the distillation was 1.089 at 11.25° falling to 1.062 at 46.2° and to an extrapolated value of 1.025 at 100°. Specially efficient fractionation columns are therefore essential for such separations. Huffmann and Urey [10] in one such column obtained water containing 0.85 per cent $H_2^{18}O$. Stedman operated another with a resultant small separation.

Among the heavier elements the early work of Brönsted and Hevesy [11] should be recalled. By a process of fractional evaporation from a liquid mercury

[1] T. I. Taylor and H. C. Urey, *ibid.*, **6**, 439 (1938).

[2] G. N. Lewis and R. T. Macdonald, *J. Am. Chem. Soc.*, **58**, 2519 (1936).

[3] W. H. Keesom and H. van Dijk, *Proc. K. Akad. Wetensch. Amsterdam*, **34**, 42 (1931); **37**, 615 (1934).

[4] E. R. Smith, *J. Chem. Phys.*, **2**, 298 (1934).

[5] H. C. Urey, F. G. Brickwedde and G. M. Murphy, *Phys. Rev.*, **39**. 164, 864 (1931); **40**, 1 (1932).

[6] R. Klar and A. Krauss, *Naturwiss.*, **22**, 119 (1934); D. F. Stedman, *Can. J. Research*, **13**, 114 (1935).

[7] M. H. Wahl, J. R. Huffmann and J. A. Hipple, *J. Chem. Phys.*, **3**, 434 (1935).

[8] G. N. Lewis and R. E. Cornish, *J. Am. Chem. Soc.*, **55**, 2616 (1933).

[9] H. C. Urey and M. H. Wahl, *J. Chem. Phys.*, **3**, 411 (1935).

[10] J. R. Huffmann and H. C. Urey, *Ind. Eng. Chem.*, **29**, 531 (1937).

[11] J. N. Brönsted and G. Hevesy, *Z. physik. Chem.*, **99**, 189 (1921).

surface to a liquid air cooled surface in a vacuum, these authors ultimately obtained two mercury fractions whose density in terms of normal mercury as unity showed displacements of $\pm$ 0.00025. Hönigschmid and Birckenbach [1] used the same method to obtain displacements of $+$ 0.02 and $-$ 0.05 units in the atomic weight. Harkins and his collaborators [2] in early experiments produced similar changes of $\pm$ 0.05 unit and, with improved techniques, two samples of as much as 100 g. with a total density difference of 0.189 unit. Chlorine was displaced 0.02 atomic weight unit by evaporation of aqueous hydrochloric acid solutions by Brönsted and Hevesy. Zinc was enriched in the same manner by Egerton and Lee [3] and the isotopes of potassium were partially displaced by Hevesy.[4] The β-ray activity was found to be increased in the heavier fraction. It is now known that the activity is a property of the isotope ^{40}K.[5]

(44) **Separation by Chemical Exchange Methods:** Experience obtained with the hydrogen isotopes in a variety of exchange reactions and comparison of the experimental data with theoretical computations based upon statistical mechanics, with due attention to the effects caused by differences in zero-point energy, served to indicate that chemical exchange methods might be employed for isotopic separations. Systematic exploration of the several possibilities with isotopes other than those of hydrogen was made theoretically by Urey and Greiff.[6] For example, the equilibrium between liquid water and gaseous carbon dioxide,

$$C^{16}O_2 + 2H_2^{18}O = C^{18}O_2 + 2H_2^{16}O,$$
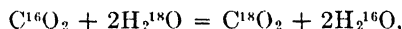
was shown by calculation to give a separation factor of 1.047 at 0° favoring the concentration of ^{18}O in the carbon dioxide. The experimental work on the concentration of ^{18}O in the electrolysis experiments provided some indication that this equilibrium was influencing the experimental results since the usual method of removing alkali from the solution involved saturation of the electrolyte with carbon dioxide. The separation factor was experimentally confirmed in Urey's laboratory.[7] Table XIII summarizes some of the separation factors of such isotope exchange reactions.

The separation factors are small and therefore, for practicable separations, they must be multiplied in effect. This is achieved by continuous operation of the exchange reaction with a counter current flow of liquid and reacting gas, using the technique of the fractionation column. For a column equivalent to n single exchange units the overall separation factor becomes α^n where α is the single separation factor. The chemical exchange method has proved especially

[1] O. Hönigschmid and L. Birckenbach, *Ber.*, **56B**, 1219 (1923).

[2] Harkins and Madorsky, *J. Am. Chem. Soc.*, **45**, 591 (1923); Harkins and Mortimer, *Phil. Mag.*, **6**, 601 (1928).

[3] A. S. Egerton and W. B. Lee, *Proc. Roy. Soc.*, [A], **103**, 499 (1923).

[4] G. Hevesy and Logstrup, *Z. anorg. Chem.*, **171**, 1 (1928).

[5] W. R. Smythe and Hemmendinger, *Phys. Rev.*, **51**, 178 (1937).

[6] H. C. Urey and L. J. Greiff, *J. Am. Chem. Soc.*, **57**, 321 (1935).

[7] L. A. Webster, M. H. Wahl and H. C. Urey, *J. Chem. Phys.*, **3**, 129 (1935).

TABLE XIII

SEPARATION FACTORS FOR ISOTOPE EXCHANGE REACTIONS

(a) Gaseous Exchange Reactions

Reaction	Equilibrium Constant at 298.1° K
$\frac{1}{2}S^{16}O_2+H_2^{18}O = \frac{1}{2}S^{18}O_2+H_2^{16}O$	1.028
$\frac{1}{2}C^{16}O_2+H_2^{18}O = \frac{1}{2}C^{18}O_2+H_2^{16}O$	1.054
$\frac{1}{2}^{16}O_2+H_2^{18}O = \frac{1}{2}^{18}O_2+H_2^{16}O$	1.020
$^{13}CO+^{12}CO_2 = ^{12}CO+^{13}CO_2$	1.086
$\frac{1}{2}^{35}Cl_2+H^{37}Cl = \frac{1}{2}^{37}Cl_2+H^{35}Cl$	1.003
$\frac{1}{2}^{14}N_2+^{15}NO = \frac{1}{2}^{15}N_2+^{14}NO$	1.015
$^{6}LiH+^{7}Li = ^{7}LiH+^{6}Li$	1.025

(b) Two Phase Exchange Reactions

Reaction	Equilibrium Constant at 298.1° K	
	Calculated	Observed
$^{15}NH_3(g)+^{14}NH_4^+(aq.) = ^{14}NH_3(g)+^{15}NH_4^+(aq.)$	1.033	1.023
$H^{12}CN(g)+^{13}CN^-(aq.) = H^{13}CN(g)+^{12}CN^-(aq.)$	1.026	1.013
$HC^{14}N(g)+C^{15}N^-(aq.) = HC^{15}N(g)+C^{14}N^-(aq.)$	1.003	<1.0
$^{34}SO_2(g)+H^{32}SO_3^-(aq.) = ^{32}SO_2(g)+H^{34}SO_3^-(aq.)$		1.012

useful in the separation of the nitrogen and the carbon isotopes and, to a minor degree, the isotopes of sulfur.

For the nitrogen isotopes use was made of the exchange reaction between ammonia gas and ammonium ion, the latter in solution as the nitrate:

$$^{15}NH_3(g) + {}^{14}NH_4^+(sol.) \rightleftharpoons {}^{14}NH_3(g) + {}^{15}NH_4^+(sol.).$$
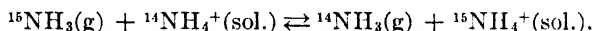
The process consists of a flow of the liquid phase downward through a column, the liberation of the ammonia by addition of sodium hydroxide and subsequent boiling, and the return of the ammonia upward through the column. In operation ^{15}N is transported down the column since it concentrates in the liquid phase, and, when a steady state has been reached under conditions of total reflux at the bottom with a very large reservoir of material at the top, there will be an exponential distribution of ^{15}N in the working material through the column. The equilibrium constant of the reaction process is about 1.023.

Urey, Huffmann, Thode and Fox[1] produced a 6.5-fold change in concentration, or 2.5 per cent ^{15}N using ammonium sulfate in a single fractionating column. These data suggested an arrangement of several fractionating columns in cascade, such that a smaller second column operates on a fraction of the product from the first column, a third a product from the second and so on. Economy of time can thereby be secured. The sizes of the columns are dependent on the enrichment factor secured in the first column. With an n-fold increase in concentration of the desired isotope in the first column, then $1/n$th

[1] H. C. Urey, Huffmann, H. G. Thode and Fox, *J. Chem. Phys.*, **5**, 856 (1937).

of the product from the first unit should be fed to the second column and the remainder stripped in a suitable stripper using alkali to liberate the ammonia which then returns to the column.   If the second unit is so chosen in size as to produce a further n-fold increase in the isotope concentration, again $1/n$th should go forward to the third column and the residue to the second stripping unit.   With three such units the isotopic concentration would become n^3-fold and for s such units n^s-fold.   Thus arranged, the columns in cascade have approximately the same transport in each unit as the system approaches a steady state, so long as the concentrations of ^{15}N in gas and liquid are not too large.   When this is no longer true the rate of flow must be increased to keep the transport constant.

The cascade principle was tested by Thode and Urey,[1] a first unit consisting of 24 meters of glass column, 7 cm. in diameter, in four 4.5 meter sections, each packed with 6-mm. Berl saddles.   A second unit consisted of 12 meters of packed column, 2.2 cm. in diameter and the third unit of 7.5 meters of column, 1 cm. inside diameter packed with glass spirals (Fig. 15).   Ammonium nitrate was used because of its high solubility.   A ten-fold increase in ^{15}N concentration was attained in units 2 and 3 with feeds of 7.5 cc. and 0.85 cc. per minute respectively of liquid product (60 per cent ammonium nitrate solution) from the preceding unit.   With a feed rate of 70 cc. per minute to unit 1 and the stated rates in units 2 and 3 with an operating pressure of 5 cm. in the first unit and 9 cm. in the second unit the enrichments obtained, at the steady state, are shown in Table XIV.   After maximum concentrations were reached the apparatus produced, in 4 days, 8.8 grams of 70.6 per cent ^{15}N removed as nitrate from the system every twelve hours.

TABLE XIV

ENRICHMENT OF ^{15}N IN AMMONIUM NITRATE-AMMONIA EXCHANGE REACTION

Unit	Enrichment Factor	Percentage ^{15}N
1	7.04	2.61
2	8.7	18.9
3	11.5	72.8
Over-all	702.	

To concentrate ^{13}C the exchange reaction between carbon dioxide and bicarbonate ion would be the most convenient but Urey found the reaction to be slow and failed to catalyze the reaction in a satisfactory and continuous manner. Urey and his co-workers therefore finally turned to the use of the hydrogen cyanide-cyanide reaction, $H^{12}CN(g) + {}^{13}CN^-(aq) = H^{13}CN(g) + {}^{12}CN^-(aq)$, to concentrate heavy carbon.   The ^{13}C concentrates in the gas phase.   The cascade process developed for nitrogen is therefore used in reverse with the small units at the top, the larger unit feeding more concentrated samples of $H^{13}CN$ to the bottom of the smaller units.   The arrangement of the two-stage

[1] H. G. Thode and H. C. Urey, *ibid.*, **7**, 34 (1939).

fractionation units used by Urey and his co-workers [1] is shown in Fig. 16.   The larger unit 1 changed the carbon isotope ratio by a factor of about 5.   The second unit changed the ratio by a factor of about 6.   Concentrations as high
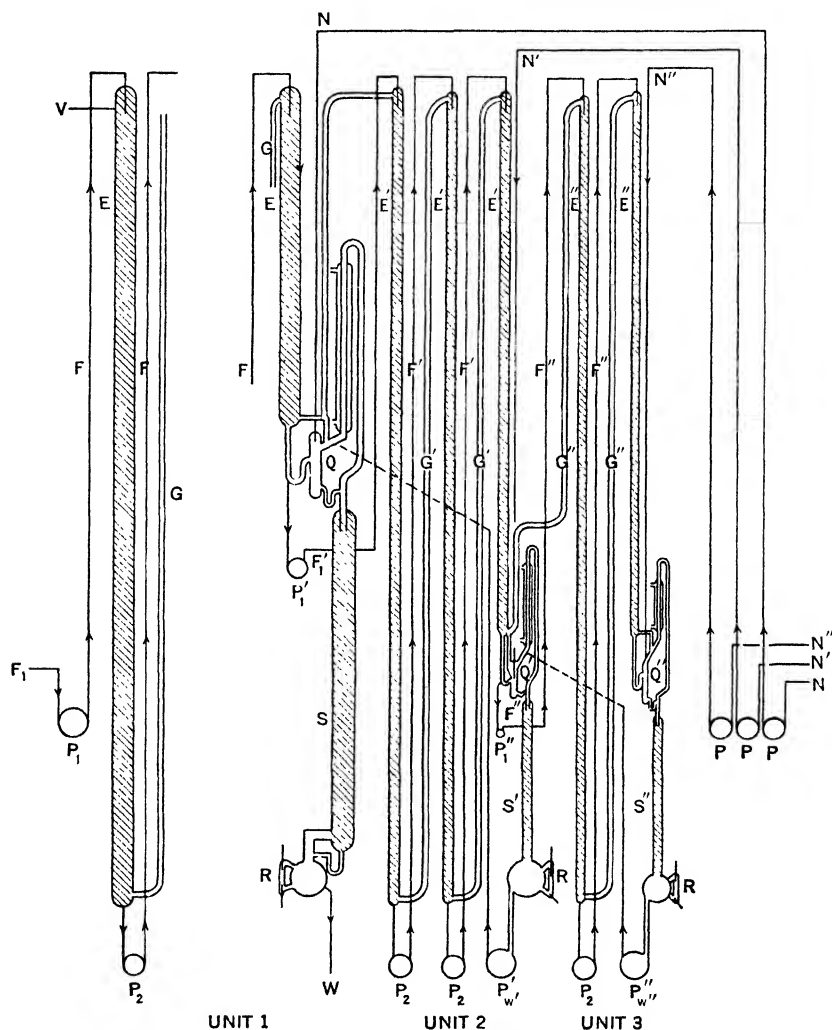

Fig. 15.   Complete Apparatus as used in the Separation of the Nitrogen Isotopes

as 22 per cent of ^{13}C have been produced at a rate of 0.1 g. of ^{13}C per 24 hours. Polymerization of the hydrogen cyanide is troublesome unless reduced to negligible proportions by the addition of sodium sulfide to the solutions.

[1] C. A. Hutchison, D. W. Stewart and H. C. Urey, *ibid.*, **8**, 532 (1940).

The concentration of ^{34}S by the chemical exchange method has also been effected.[1] The reaction used was that between sulfur dioxide gas and a solution of sodium bisulfite. Using three fractionation units in the usual cascade arrangement, sulfur containing 25 per cent of ^{34}S could be secured at the rate of 3.2 g. per day. An experimental value for the simple process fractionation factor α of 1.012 was obtained in room temperature operation, the heavy sulfur
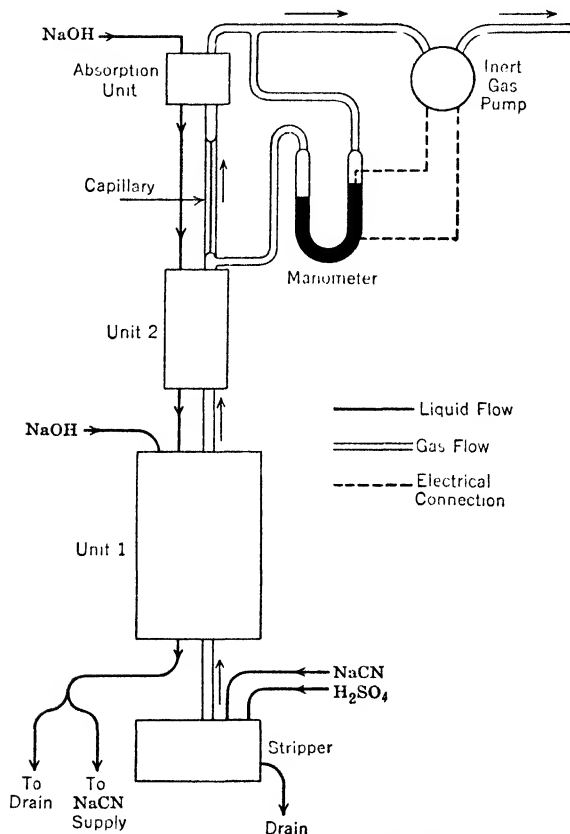

Fig. 16.   Arrangement of Fractionation Units in the Separation of Carbon Isotopes

concentrating in the liquid phase. Heavy sulfur thus becomes available for tracer experiments requiring long time intervals of experimentation. Radioactive sulfur has similar applicability in tracer experiments of limited duration.

Reference has already been made to the experiments of Lewis and MacDonald who used the exchange reaction between lithium amalgam and lithium ion dissolved in alcohol for the fractionation of lithium isotopes. Taylor and

[1] D. W. Stewart and K. Cohen, *ibid.*, **8**, 904 (1940).

Urey [1] have also used the difference in the exchange reaction between water solutions of alkali metal ions and solid zeolites as a means of concentrating the isotopes of lithium, nitrogen (ammonium ion) and potassium. Lithium ions displace sodium ions from a sodium zeolite, the ^6Li more readily than the ^7Li ions so that the leading sample was enriched in ^7Li. Displacement of exchanged lithium zeolite by sodium chloride removed ^7Li more rapidly so that ^6Li was enriched in the trailing sample. Changes of 25 per cent in the normal abundance of heavy lithium and of 10 per cent with nitrogen and potassium have been thus secured. With the latter elements the heavier isotope is preferentially concentrated in the zeolite.

(45) **Isotope Species and Optical Spectra:** Optical spectra of atoms and molecules may be used to supplement the data of mass spectrography. The aid thus obtained has been of prime significance in the recent development in this field. Optical spectra have been employed not only for the discovery of isotopes but also for the determination of abundance ratios. It will be sufficient, at this juncture, to indicate the lines upon which this work has developed, leaving to subsequent chapters the detailed elucidation of the fundamental principles involved.

The energy of a molecule can be expressed, apart from its energy of translation, in terms of its constituent rotational, vibrational and electronic energies,

$$E = E_r + E_v + E_e. \tag{45.1}$$

Spectra resulting from transitions between two energy levels can be analyzed in terms of the changes in these several forms of energy. In each type of energy change there will be an isotope effect due to the differences of isotopic masses in the molecule. That due to an electronic transition $E_e' - E_e''$ will in general be small and, thus far, it has not been used. Associated with an electronic change there are vibrational and rotational changes which will show isotope effects in the electronic bands as they will, also, in pure vibration-rotation transitions. The energies of a diatomic molecule due to vibration and rotation are representable by equations of the form

$$E_v = hc\omega_e(v + \tfrac{1}{2}) - x_e\omega_e(v + \tfrac{1}{2})^2 + \cdots \tag{45.2}$$

and

$$E_r = hc[B_vJ(J + 1) + D_vJ^2(J + 1)^2 + \cdots]. \tag{45.3}$$

The vibrational quantum number v may have values of 0, 1, 2, 3, $\cdots$; ω_e is the frequency of vibration of the molecule expressed in cm.$^{-1}$ ($1/\lambda$) and $c\omega_e = \bar{\nu}$ the frequency of vibrations in sec.$^{-1}$ about the equilibrium position in the particular vibrational state, c being the velocity of light and h the Planck constant. The second and higher terms take account of the anharmonicity of the molecule. Since the frequency of vibration ω of the nuclei depends upon the reduced mass, μ, $\omega_e \propto \mu^{-1/2}$ where $\mu = m_1m_2/(m_1 + m_2)$, it is apparent how the different

[1] T. J. Taylor and H. C. Urey, *ibid.*, **6**, 429 (1938).

isotopic masses of a given element will affect the value of ω_e and therefore the spectra.

The rotational energy expression contains, in addition to the rotational quantum number J with integral values of 0, 1, 2, 3, 4 etc., the constant $B_v = h/8\pi^2 c I_v$. Here I_v is the effective moment of inertia of the molecule in the given vibrational state. This quantity is given by the expression $m_1 m_2 (r_1 + r_2)^2/(m_1 + m_2) = \mu r^2$ where m_1 and m_2 are the masses, r_1 and r_2 their distances from the center of gravity of the molecule, r the distance apart of the atoms in the molecule. D_v is a small negative correction also expressible in terms of I_v. The effect of these two constants in the energy expression is to introduce a corresponding isotope effect into the rotational spectra when one of the atoms of the molecule can have different isotopic masses.

In atomic spectra of hydrogen-like atoms there will be an isotope effect due to the effect of changes in nuclear mass M_i on the frequency of the transition from the n' to the n'' quantum state, given by the Bohr equation,

$$\nu = Z^2 Rc \left(\frac{1}{n''^2} - \frac{1}{n'^2} \right), \qquad (45.4)$$

where Rc has the value $2\pi^2 m e^4 \left/ \left(1 + \frac{m}{M_i} \right) h^3 \right.$ where m is the electronic mass

and e the electronic charge, Z representing the nuclear charge. It was this shift in frequency which was used by Urey, Brickwedde and Murphy [1] to characterize their discovery of the deuterium isotope in hydrogen.

One further effect due to isotopes in spectra is to be attributed to the nuclear spin. The spin moments of isotopic nuclei may differ and, as a consequence, the spectra may differ. The effect is best indicated with reference to the homonuclear molecules hydrogen and deuterium. In the former the two nuclei have each a spin of $\frac{1}{2}$ giving resultant nuclear moments of 1 and 0. Molecules with moment 1 are known as orthohydrogen. They have three states of equal probability. Molecules with moment 0 are known as parahydrogen and there is only one state. Ordinary hydrogen is a mixture of orthohydrogen and parahydrogen in the ratio of 3 : 1. Parahydrogen molecules possessing antiparallel nuclear spins have even rotational quantum numbers $J = 0, 2, 4, 6$. Orthohydrogen with parallel spins have odd rotational quantum numbers $J = 1, 3, 5$. This ratio of the two forms results in corresponding alternating intensities in the molecular spectra. In the isotopic homonuclear molecule D_2 the isotopic nucleus D has a spin of unity. The molecule exists in two states, the ortho-states with even rotational quantum numbers, the para- with odd rotational quantum numbers, the ratio at high temperatures being 2 ortho : 1 para with corresponding alternations in intensity in the spectra. Heteronuclear molecules such as HD and $^{35}Cl^{37}Cl$ show no alternation of intensities in their spectra.

[1] H. C. Urey, F. G. Brickwedde and G. M. Murphy, *Phys. Rev.*, **39**, 164, 864 (1931); **40**, 1 (1932).

In the atomic spectra the hyperfine structure of the spectral lines depends to a certain extent upon the nuclear spin and may therefore change from isotope to isotope.

(46) **Isotope Discovery from Spectral Data:** Hydrogen chloride is an example from the spectra of which data on isotopes have been derived. As early as 1919 the vibration-rotation bands of this compound were examined by Imes [1] who found that the rotational components were broadened on the side of lower frequencies where a satellite due to $H^{37}Cl$ should be found. The interpretation of the broadening in this sense was given by Loomis [2] and by Kratzer [3] in 1920. The intensive development of infra-red spectroscopy notably that which has been achieved in the University of Michigan has permitted the complete resolution of the isotopic bands due to the two chlorine isotopes. Not only has the calculated vibrational separation of 4 cm.$^{-1}$ been verified but the small increase of this with increasing values of the rotational quantum number J due to the additional rotational isotope effect has been found in best agreement with theoretical calculation. [4]

A discovery of isotopes from molecular spectra which had far-reaching effects in physical science was the observation of Giauque and Johnston [5] that the spectra of atmospheric air showed that the molecules of ordinary oxygen do not consist exclusively of atoms of mass 16, but also contain atoms of masses 17 and 18. The natural abundances of the three were found to be 99.76, 0.04 and 0.20 per cent. The correlation of the mass ratios H : O obtained by mass-spectrographic and ordinary chemical methods revealed a discrepancy, when account was taken of the constituents of masses 17 and 18 in oxygen, such that, as pointed out by Birge and Menzel, [6] the existence of a hydrogen isotope of mass 2 was indicated, present to the extent of 1 part in 5000 in ordinary hydrogen. This isotope was successfully demonstrated by Urey, Brickwedde and Murphy. [7]

The complexity of oxygen also raised doubts with respect to the element carbon. These doubts were resolved by the discovery by Birge and King [8] of the carbon isotope of mass 13, with an abundance of 1.1 per cent, from a study of the band spectra of gaseous carbon compounds, among others that of carbon monoxide.

<div align="center">NUCLEAR PROCESSES</div>

(47) **Nuclear Transformations by α-Particles:** The transformation of stable nuclei was first achieved by Rutherford [9] in a series of researches beginning in

[1] Imes, *Astrophys. J.*, **50**, 251 (1919).

[2] Loomis, *ibid.*, **52**, 248 (1920).

[3] Kratzer, *Z. Physik*, **3**, 460 (1920).

[4] J. D. Hardy and G. B. B. M. Sutherland, *Phys. Rev.*, **41**, 471 (1932).

[5] W. F. Giauque and H. L. Johnston, *Nature*, **123**, 318, 831 (1929).

[6] R. T. Birge and D. H. Menzel, *Phys. Rev.*, **37**, 1670 (1931).

[7] H. C. Urey, F. G. Brickwedde and G. M. Murphy, *ibid.*, **39**, 164, 864 (1932).

[8] R. T. Birge and A. S. King, *Nature*, **124**, 127, 182 (1929); R. T. Birge, *Phys. Rev.*, **34**, 379 (1929).

[9] E. Rutherford, *Phil. Mag.*, **37**, 581 (1919).

1919, using the swift α-particles from RaC' as the bombarding source. These α-particles have a range of 6.97 cm. in air. The method employed was to determine, by observation of the scintillations produced on a zinc sulfide screen through metal foils of calibrated stopping powers, the ranges of particles causing the scintillations. Thus, with an apparatus filled with hydrogen, scintillations were observed when the combined effects of the gas atmosphere and absorption screens were equivalent to 29 cm. of path in air at atmospheric pressure and room temperature. Admixture of carbon dioxide with the hydrogen did not change this range which was evidently associated with interaction between the α-particles and hydrogen nuclei. The curve of scintillations against range cut the range axis for zero scintillations at 29 cm. The particles producing the scintillations were evidently hydrogen nuclei or protons, whose energies are derived from elastic collisions with the more massive helium nuclei.

With oxygen as bombarded gas only particles of 26 cm. range were observed and these, it was assumed, came from proton impurities in the apparatus. With nitrogen in the form of air, on the other hand, particles with a range equivalent to 40 cm. in air were obtained. Since such ranges could not arise by elastic impacts with helium nuclei of 7 cm. range it was assumed that the particles with 40 cm. range were protons shot from the nitrogen nucleus by the disintegration process,

$$_{2}^{4}\text{He} + {}_{7}^{14}\text{N} = {}_{8}^{17}\text{O} + {}_{1}^{1}\text{H}.$$
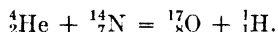
Since the energy of these protons was greater than those observed with hydrogen it followed that the energy of the interaction, He + N, must have contributed to the kinetic energy of the proton expelled. With aluminum foil as the bombarded material the range of the protons reached 90 cm., indicating an even larger conversion of inter-nuclear energy. The particles produced were then shown to be protons by a study of their behavior in electro-magnetic and electrostatic fields.

With Chadwick, Rutherford [1] demonstrated the production of swift hydrogen nuclei by collision of α-particles with boron, nitrogen, fluorine, neon, sodium, aluminum, silicon, phosphorus, sulfur, chlorine, argon and potassium. In the same period of time Kirsch and Pettersson [2] investigated the production of hydrogen nuclei not only from the light elements just cited but also from ten heavy elements including iron and copper. They claimed the production of nuclei from lithium, beryllium, carbon and oxygen with which Rutherford and Chadwick had obtained negative results.[3] The helium nucleus gave negative results to both sets of workers.

[1] E. Rutherford and J. Chadwick, *Phil. Mag.*, **42**, 809 (1921); **44**, 417 (1922); **48**, 509 (1925); *Proc. Phys. Soc. London*, **36**, 417 (1924); J. Chadwick, *ibid.*, **2**, 1056 (1926).

[2] H. Pettersson and G. Kirsch, Atomzertrümmerung, Akad. Verlagsges., Leipzig, 1926.

[3] M. S. Livingston and H. A. Bethe (*Rev. Mod. Phys.*, **9**, 295 (1937)) conclude that "in face of the existing evidence we are forced to eliminate these data from Vienna."

The data obtained by the scintillation method were confirmed subsequently by the cloud chamber method.

(48) **Energy Exchanges in Elastic Impacts:** For a head-on collision of two particles m_1 and m_2 travelling with velocities v_1 and v_2 respectively the principle of conservation of momentum demands that

$$m_1v_1 + m_2v_2 = m_1v_1' + m_2v_2', \tag{48.1}$$

where v_1' and v_2' are the respective velocities after the collision process. If we assume that the collision complex before separation of the masses has a single velocity u it follows from conservation considerations that

$$m_1v_1 + m_2v_2 = (m_1 + m_2)u = m_1v_1' + m_2v_2'. \tag{48.2}$$

From this we derive

$$u = \frac{m_1v_1 + m_2v_2}{m_1 + m_2}. \tag{48.3}$$

Conservation also demands that

$$m_1u_1 - m_1v_1 = m_1v_1' - mu = m_2v_2 - m_2u = m_2u - m_2v_2'; \tag{48.4}$$

from which it follows that

$$v_1' = 2u - v_1; \qquad v_2' = 2u - v_2 \tag{48.5}$$

or

$$v_1' = 2\frac{m_1v_1 + m_2v_2}{m_1 + m_2} - v_1; \qquad v_2' = 2\frac{m_1v_1 + m_2v_2}{m_1 + m_2} - v_2. \tag{48.6}$$

For the special case in which one particle when struck is effectively at rest, i.e., $v_2 = 0$, then

$$v_2' = 2\frac{m_1v_1}{m_1 + m_2}. \tag{48.7}$$

For an elastic collision between a moving particle m_1 and one at rest m_2 in which the particles m_1 and m_2 after collision leave at angles ψ and θ respectively to the original direction of motion of m_1 the conservation rules demand that

$$m_1v_1 = m_1v_1' \cos \psi + m_2v_2' \cos \theta, \tag{48.8}$$

$$0 = m_1v_1' \sin \psi + m_2v_2' \sin \theta, \tag{48.9}$$

$$m_1v_1^2 = m_1v_1'^2 + m_2v_2'^2. \tag{48.10}$$

These yield for the velocity v_2'

$$v_2' = \frac{m_1}{m_1 + m_2} \cos \theta. \tag{48.11}$$

Thus, a head on collision between an α-particle and a proton at rest will give

a maximum velocity to the proton ($\theta = 0$; $\cos \theta = 1$). The velocity in terms of that of the α-particle will be

$$v_p = 2 \frac{4}{4 + 1} v_\alpha = 1.6 v_\alpha. \tag{48.12}$$

We assume with Bohr that the range of a charged particle in a given medium is directly proportional to its mass and inversely proportional to its charge. Further, according to the empirical relation, due to Geiger, the range varies directly as the third power of the velocity. Thus:

$$R_\alpha = k' v_\alpha^3,$$

whence, since the charge on the α-particle is $2e$,

$$R_\alpha = k v_\alpha^3 \frac{m_\alpha}{4e^2}, \tag{48.13}$$

whilst the corresponding range for the proton is

$$R_p = k v_p^3 \cdot \frac{m_p}{e^2}. \tag{48.14}$$

Using the above relation between v_α and v_p it follows that

$$\frac{R_p}{R_\alpha} = \frac{(1.6)^3 v_\alpha^3}{v_\alpha^3} \cdot \frac{4}{1} \times \frac{1}{4} = 4.1. \tag{48.15}$$

Since the range of the α-particles from RaC' in the Rutherford experiment was 6.97 cm., it follows that the maximum range of the protons from an elastic collision will be $4.1 \times 6.97 = 28.58$ cm. in agreement with observation.

(49) **Energy Relations in Inelastic Impacts:** Ranges of protons observed as a result of inelastic impacts between α-particles and heavier atoms obviously depend also on the energies of the nuclear transformation processes. From the Einstein relation, $E = mc^2$, where c is the velocity of light, 2.998×10^{10} cm. per sec., energy being expressed in ergs and the mass in grams, a mass of one gram is equivalent to an energy of 9×10^{20} ergs, somewhat more than 2×10^{13} calories, approximately 10^9 electron volts (10^3 M.e.v.).

The accurate mass spectrographic data of Bainbridge and Jordan [1] for hydrogen and helium give masses of 1.00813 and 4.00389 respectively. The formation of a helium nucleus from 4 protons results therefore in a mass loss of $4 \times 1.00813 - 4.00389 = 0.02863$ mass units or $0.0286 \times 9 \times 10^{20} = 0.257 \times 10^{20}$ ergs per mole, or 6×10^{11} cal. per mole. The mass of the electron is $1/1837 = 0.00055$ on the atomic weight scale or $0.00055 \times 9 \times 10^{20} = 4.95 \times 10^{17}$ ergs $= 1.2 \times 10^{10}$ cals. $= 0.5 \times 10^6$ e.v. $= 0.5$ M.e.v.

[1] K. T. Bainbridge and E. B. Jordan, *Phys. Rev.*, **49**, 883 (1936); **50**, 98 (1936); **51**, 384, 385 (1937).

For a process involving an inelastic collision such as the interaction of α-particles and nitrogen nuclei,

$$^{14}_{7}N + {}^{4}_{2}He = {}^{17}_{8}O + {}^{1}_{1}H,$$
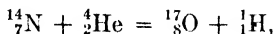
with a stationary nitrogen atom, the energy of the α-particle together with energy produced or consumed in mass change (ΔE) is equal to the energies of the nuclei formed. In the present case it is found by measurement that energy is bound in the process to the extent of 1.26 M.e.v.[1] Since $\Delta E = \Delta m \cdot c^2 = 9 \times 10^{20} \Delta m$ ergs,

$$= \frac{6.02 \times 10^{23}}{300} \text{ e.v.} = \frac{6.02 \times 10^{23} \times 4.80 \times 10^{-10}}{300} V$$

$$V = \frac{300 \times 9 \times 10^{20} \Delta m}{6.02 \times 10^{23} \times 4.80 \times 10^{-10}} = 931.4 \times 10^6 \Delta m \text{ volts}$$

or

$$\Delta E = 1.26 \times 10^6 \text{ e.v.} = 931.4 \times 10^6 \Delta m,$$

whence

$$\Delta m = 0.00135 \text{ mass unit.}$$

Since N = 14.0075, He = 4.0039 and H = 1.0081 it follows that the mass of the oxygen isotope ^{17}O should be

$$^{17}O = 14.0075 + 4.0039 + 0.00135 - 1.0081.$$
$$= 17.0046.$$

This isotope of oxygen has not yet been measured accurately by mass spectrographic methods.

(50) **Bombarding Agents for Nuclear Transformations:** Prior to 1932 only α-particles from radioactive sources were employed in the production of nuclear transformations. In that year, as has already been stated, the existence of the neutron was recognized by Chadwick and the possibility of employing such particles in the problem of nuclear reactions, due to the absence of charge, was immediately obvious. In the same year, the first experiments of Cockcroft and Walton,[2] in England, to impart high velocities to protons were brought to a successful conclusion. Protons having velocities of 7×10^5 e.v. were obtained in current strengths of 10^{-5} amp. and larger currents at somewhat smaller voltages. Even with these relatively small potentials, due to the resonance phenomenon already discussed in connection with the Gamow-Gurney-Condon theory, it was found possible to bombard the lithium nucleus with the production of disintegration products having a range of 8.4 cm. The reaction occurring,

$$^{7}_{3}Li + {}^{1}_{1}H = {}^{4}_{2}He,$$

[1] M. S. Livingston and H. A. Bethe, *Rev. Mod. Phys.*, 9, 375 (1937).

[2] J. C. Cockcroft and E. T. S. Walton, *Proc. Roy. Soc.*, [**A**], **136**, 619 (1932); **137**, 229 (1932).

releases considerable energy by reason of the mass loss involved. Increase in velocity of the protons was shown [1] markedly to increase the transformation, a ten-fold increase resulting from an increase in velocity from 1×10^5 to 2×10^5 e. volts. Simultaneously with the development of the high potential apparatus (See Section 56) by Cockcroft and Walton in England and by Crane, Lauritsen and Soltan [2] in California Institute of Technology, Lawrence in the University of California was developing the new technique of production of ion sources at high potentials embodied in the cyclotron. The availability of heavy hydrogen, consequent upon Urey's discovery of this isotope, presented another high speed projectile, the deuteron ($_1^2H$; $_1^2D$), for nuclear transformation. From its nuclear structure, composite of a proton and a neutron, interesting properties of the particle could be anticipated and were found in nuclear transformations. With the ^6Li isotope, the nuclear reaction,

$$_3^6Li + _1^2D = 2\,_2^4He,$$
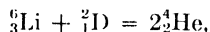
results while, with the ^7Li isotope, a neutron $_0^1n$ is produced in addition,

$$_3^7Li + _1^2D = 2\,_2^4He + _0^1n.$$
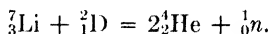
With the modern forms of the cyclotron, permitting the production of charged ions with velocities up to many M.e.v., it is also possible to use helium ions as the cyclotron beam, thus to check independently observations with α-particles from radioactive sources, and to produce concentrations of these projectiles greater than can be secured from available radioactive sources.

In addition to the material particles, neutrons, protons, deuterons and α-particles, short-wave photons, the γ-rays, have also been employed for nuclear transformations. The production of γ-rays by nuclear disintegration was recognized early in the development of the study of radioactivity. Nuclear transformation with the aid of high energy γ-rays represents therefore a reversal of this change. Chadwick and Goldhaber [3] utilized such a reaction to reveal the structure of the deuteron. With the hard γ-rays from ThC″, with an energy of 2.6 M.e.v., deuterons are converted into protons and neutrons

$$_1^2D + h\nu(\gamma) = _1^1H + _0^1n,$$
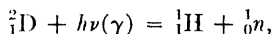
a reaction from which the mass of the neutron may be deduced (Section 52).

(51) **The Neutron. Discovery:** It was observed by Bothe and Becker [4] in 1930 that the bombardment of light elements such as lithium and beryllium by α-particles yielded a very penetrating γ-radiation of short wave length. Irène Curie and Joliot then found [5] that the radiation, especially from beryllium,

[1] M. L. Oliphant and E. Rutherford, *Proc. Roy. Soc.*, [A], 141, 259 (1933); E. O. Lawrence, M. S. Livingston and M. G. White, *Phys. Rev.*, 42, 150 (1932).

[2] H. R. Crane, C. C. Lauritsen and A. Soltan, *ibid.*, 45, 507 (1934)

[3] J. Chadwick and M. Goldhaber, *Nature*, 134, 237 (1934).

[4] W. Bothe and H. Becker, *Z. Physik*, 66, 289 (1930).

[5] I. Curie and F. Joliot, *Compt. rend.*, 193, 1412, 1415 (1931); 194, 273, 708, 876 (1932).

set free protons from materials such as paraffin containing large quantities of hydrogen. This behavior led Chadwick to suggest [1] that, in addition to the γ-radiation, there must also be present a corpuscular constituent without electric charge. This he demonstrated in the following manner. An α-particle source from polonium on a silver target was allowed to impinge on a beryllium source in an evacuated container. The secondary radiation thus produced passed through the walls of the container to an ionization chamber closed with aluminum foil equivalent to 4.5 cm. of air. The ionization produced in the chamber was measured. If now a 2 mm. thick sheet of paraffin was interposed between the source and ionization chamber the number of recorded ions increased considerably. These were due to the protons produced in the paraffin by the secondary radiation from the beryllium and their energies could be determined by interposition of aluminum screens of suitable thicknesses. Maximum proton velocities of 3×10^9 cm. per sec. or energies equal to 5.7×10^6 e. volts were recorded. Further, the effect of the secondary radiation from the beryllium was but little weakened when lead was interposed between the beryllium source and the paraffin. This definitely ruled out α- and β-particles as the cause of the proton formation in the paraffin. It was further shown by the Joliots that a strong magnetic field did not influence the intensity of the proton-producing constituent. This left only γ-quanta or an uncharged particle. The enormous energies which the former must possess to release protons of the energies indicated appeared to exclude γ-radiation. Chadwick concluded therefore that the radiation from the beryllium contained neutrons. Experiments with the Wilson cloud chamber by the Curie-Joliots,[2] Feather,[3] Meitner [4] and Philipp [5] confirmed this. Neutrons passed to the interior of the chamber from outside and, since they do not markedly ionize, their paths are not visible. Protons from a paraffin sheet within the chamber are, however, visible as tracks from the paraffin source. Chadwick was able to determine the approximate mass of the neutron by comparison of the maximum velocities of protons and nitrogen nuclei produced by the impacts of neutrons in hydrogen and nitrogen respectively. By the principle of conservation of energy and momentum upon impact, assuming hydrogen and nitrogen initially at rest, the velocities will be for a neutron of mass M and velocity v,

$$u_\text{H} = \frac{2M}{M + m_\text{H}} v; \qquad u_\text{N} = \frac{2M}{M + m_\text{N}} v. \tag{51.1}$$

He concluded that, within an error of 10 per cent, the mass of the neutron was identical with that of the proton.

(52) **Properties of Neutrons:** Neutrons are uncharged particles of approximately unit mass with a unique penetrating power. Because of their lack of

[1] J. Chadwick, *Proc. Roy. Soc.*, [A], **136**, 692 (1932); **142**, 1 (1933).

[2] I. and F. Curie-Joliot, *Compt. rend.*, **194**, 708 (1932).

[3] N. Feather, *Proc. Roy. Soc.*, [A], **136**, 709 (1932).

[4] L. Meitner, *Naturwiss.*, **20**, 929 (1932).

[5] K. Philipp, *ibid.*, **20**, 929 (1932).

charge they are not influenced by the outer electrons of atomic systems but suffer collisions with nuclei, the approach of neutrons to which is not hampered by the repulsive forces operative between charged particles and nuclei. Since the size of the nucleus varies little from substance to substance and the number of nuclei per unit volume is the determining factor governing the number of neutron collisions it is obvious that, per gram of material, hydrogen-rich materials will be the most effective agents for neutron absorption. The absorption relations sharply distinguish neutrons from γ-rays. The latter are absorbed not only in proportion to the number of atoms but also in proportion to the electrons these atoms contain. Hence γ-rays are more strongly absorbed by lead than are neutrons, but in paraffin the neutrons are much more strongly absorbed. Again, because of the lack of charge, the range of neutrons will be large, several kilometers in air; even lead 30 cm. thick cuts down the neutrons from a beryllium source only some 10 per cent. For the same reason also neutrons have little ionizing influence on the atoms through which they pass. In collisions with the positive nuclei of the atoms they give up energy, especially so with the nuclei of light atoms. It is in this manner that Fermi and his collaborators reduced the speeds of neutrons by encasing the neutron source in materials such as water or paraffin, rich in hydrogen. The successive collisions finally reduced the energies of the neutrons to values comparable with those due to thermal motion. With decrease in neutron energy, the important observation was made that the cross-section of the nucleus for neutron capture was markedly increased. For fast neutrons the cross-section is of the order of 10^{-24} cm.^{2} but with slow neutrons areas from 100 to 10,000 times this value were observed.

(53) **Neutron Producing Processes:** Spontaneous radioactive change is not known to produce neutrons. Neutron emission is common from nuclei bombarded with high speed particles or γ-rays. As neutron sources of practical importance, either from the standpoint of yield, homogeneity, convenience or energy-distribution, the following reactions are the most important.

(a) *Deuteron-Deuteron Interaction:* $^2D + {}^2D = {}^3He + {}^1n$. This reaction is important because of high yield and absence of γ-radiation. Recent observations on this reaction give 1.2×10^{-7} neutron per deuteron when referred to a target of pure deuterium and a deuteron energy of 0.1 M.e.v. The neutrons produced are fairly homogeneous with energies around 2.5 M.e.v. A group of lower energy, ~ 1 M.e.v. has been considered as due to scattering of the more energetic neutrons but also as due to the ^3He nucleus being produced in an excited state.

(b) *Lithium-Deuteron Interaction:* $^7Li + {}^2D = {}^8Be + {}^1n$. Two groups of neutrons are produced with energies of 14 and 11 M.e.v. from deuterons of 0.93 M.e.v. the less energetic five-fold more intense than the more energetic. With 5.7 M.e.v. deuterons, neutron energies up to 20.8 M.e.v. in the forward direction are obtained. The angular distribution of the neutrons then agrees with the reaction $^7Li + {}^2D = 2{}^4He + {}^1n$, rather than with the formation of ^8Be.

(c) *Beryllium-Helium Interaction:* $^9Be + {}^4He = {}^{12}C + {}^1n$. The bombard-ment of beryllium by α-particles is the earliest and still an important source of neutrons due to the size and convenience of the apparatus. A mixture of beryllium metal with radium or radon is used and such mixtures are suitable as standards of comparison with other neutron sources. From 1 millicurie of radium mixed with beryllium powder the accepted value for the yield is about 25,000 neutrons per second. The range of energies is large, depending on the energies of the α-particles, is a more or less continuous distribution and reaches as high as 13 M.e.v.

(d) *Deuterium-γ-ray Interaction:* $^2D + \gamma = {}^1H + {}^1n$. This reaction is especially useful as a source of neutrons of known energy. The binding energy of the deuteron is 2.2 M.e.v. so that a γ-ray of energy E gives an available energy of $(E - 2.2)$ M.e.v., shared approximately equally by both proton and neutron.

(54) **The Mass of the Neutron:** This last interaction between a deuteron and a γ-ray is the basis of the best method of determination of neutron mass. From the Einstein relation, if the energy E ergs is employed to disintegrate a mass m_1 into masses m_2 and m_3 it follows that $m_1 + E/c^2 = m_2 + m_3$ where c is the velocity of light. The best data on the interaction of deuterons and γ-radiation, with the greatest refinements in relating proton energies to their observed ranges, yield a value for the mass of the neutron of 1.00893.[1] An independent determination of the binding energy of the deuteron which does not involve the range-energy relation gives a value 1.00895.[2]

(55) **Spin and Magnetic Moment of the Neutron:** From experiments on the scattering of neutrons by ortho- and para-hydrogen it has been concluded that the spin of the neutron is $1\frac{1}{2}$ in units of $h/2\pi$;[3] for the magnetic moment the value of -2 nuclear magnetons is obtained.[4]

(56) **Techniques for the Production of High Velocity Ions as Projectiles:**[5]

(a) *The Voltage Multiplier:* The earliest experiments of Cockcroft and Walton in the production of high speed protons used the condenser-rectifier voltage multiplier. The voltage multiplication principle of charging condensers in parallel and discharging in series across a load was employed to triple the output from a transformer supplying 60 cycle alternating current at 250 kv. Rectifier tubes, used as switches, provide a method of charging the condensers 60 times a second and thus a direct potential of about 800 kv. is provided across a final bank of three condensers, suitably mounted on insulating supports. The transformer charges a feeding condenser through two rectifiers which are conducting during one half cycle. In the next half cycle these rectifiers are non-conducting and the feeding condenser divides its charge with another

[1] H. A. Bethe, *Phys. Rev.*, **53**, 313 (1938).

[2] G. Stetter and H. Jentsch, *Z. Physik*, **110**, 214 (1938).

[3] F. G. Brickwedde, J. R. Dunning, H. J. Hoge and J. H. Manley, *Phys. Rev.*, **54**, 266 (1938).

[4] O. R. Frisch, H. von Halban and J. Koch, *ibid.*, **53**, 719 (1938).

[5] M. S. Livingston and H. Bethe, *Rev. Mod. Phys.*, **9**, 247 (1937).

condenser through a second set of rectifiers and so on until all condensers are fully charged.

The high voltage discharge tube of porcelain is continuously pumped. Canal-ray sources of protons are introduced at the high potential end, accelerated through large tubular electrodes and strike the target at the grounded end. Currents were originally about $10\mu a$. (microamperes) at 800 kv. but these have been increased to as much as $100 \mu a$.

(b) *The Cascade Transformer:* Lauritsen and Crane in Pasadena developed high voltage transformers for deep therapy X-ray tubes. Three transformers of 350 kv. are arranged in series; the primaries of the second and third transformers are activated from low voltage tertiaries at the high potential ends of the high voltage windings of the first and second transformers respectively. The second and third transformers rest on insulators permitting operation at 350 and 700 kv. above the ground potential. Currents of protons up to $20 \mu a$. at 900 kv. are obtained continuously and for short periods as much as $100 \mu a$. More recently Crane has produced currents of $250 \mu a$. at 10^6 volts (1 M.v.). These currents can be focused on a target of 1.2 cm. diameter.

(c) *The Electrostatic Generator:* Van de Graaff [1] developed the electrostatic generator. An endless belt of insulating material carries an electric charge from a high voltage rectifier to a large hollow collecting sphere, which accumulates the potential steadily. The Van de Graaff machines range from one yielding a few μa. at 80 kv. to the Round Hill installation yielding several milliamperes at 5 M.v. This principle was used successfully by Tuve, Hafstad and Dahl [2] for transmutation purposes by reason of their development of a discharge tube. They have obtained positive ion currents of 20 μa. at 1.2 M.v. The sphere is mounted on Textolite insulating supports. The discharge tube is in sections with hollow cylindrical electrodes. The voltage limit is set by the corona from the surface of the sphere. The limiting potential may be increased by the construction of electrostatic generators of smaller size but built inside tanks which can be filled with air at 6–7 atm. Ions up to 2.2 M.e.v. energy have thus been obtained.[3]

(d) *High Intensity Discharge Tube:* Oliphant and his collaborators [4] have used a high intensity discharge tube with 100 μa. of protons or deuterons accelerated to 200 kv. in a single stage from a 100 kv. transformer with a voltage doubler circuit. In later work the intensity was increased to 200 μa. The objective in this technique was a beam with high accuracy of energies.

(e) *The Cyclotron:* The most popular technique for the attainment of high energy ions is that developed by Lawrence in the University of California, known as the magnetic resonance accelerator or, more generally, the cyclotron. This has proved to be the source of the highest energies obtained by ion ac-

[1] R. J. Van de Graaff, K. T. Compton and L. C. van Atta, *Phys. Rev.*, **43**, 149 (1933).

[2] M. A. Tuve, L. R. Hafstad and O. Dahl, *ibid.*, **48**, 315 (1935); **50**, 504 (1936).

[3] R. G. Herb, D. B. Parkinson and D. W. Kerst, *ibid.*, **51**, 75 (1937).

[4] M. L. E. Oliphant and E. Rutherford, *Proc. Roy. Soc.*, [**A**], **141**, 259 (1933); **144**, 692 (1934).

celeration and the enormous results already attained are but the prelude to still higher energies in prospect. The principle invoked is the successive frequent acceleration of the ions in relatively small amounts in a low voltage high frequency field with which the ions are in resonance. The ions circulate back and forth from the interior of one electrode to the interior of the other as shown diagrammatically in Fig. 17. Two electrodes, *A* and *B*, in the form of semi-
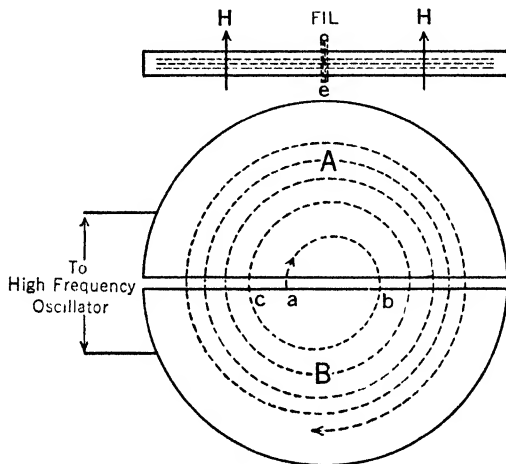

Fɪɢ. 17.   Schematic Diagram of the Lawrence Cyclotron

circular hollow plates (the dees) are mounted in a vacuum tube in co-planar fashion with their diametral edges adjacent. The system is placed between the poles of a magnet and a magnetic field, II, is introduced normal to the plane of the plates. High frequency electric oscillations are applied to the plates so that there results an oscillating electric field in the diametral region between them.

With this arrangement, it is evident that, if at one moment there is an ion in the region between the electrodes and electrode *A* is negative with respect to *B*, the ion will be accelerated to the interior of the former. Within the electrode the ion traverses a circular path because of the magnetic field, and ultimately emerges again between the electrodes, this is indicated in the diagram by the arc $a \cdots b$. If the time consumed by the ion in making the semi-circular path is equal to the half-period of the electric oscillations the electric field will have reversed and the ion will receive a second acceleration, passing into the interior of *B* with a higher velocity. Again it travels on a semi-circular path $(b \cdots c)$ but this time the radius of curvature is greater because of the greater velocity. For all velocities (neglecting variation of mass with velocity) the radius of the path is proportional to the velocity, so that the time required to traverse a semi-circular path is independent of ion velocity. Therefore, if the ion travels its first half circle in a half cycle of the oscillations it will do so on

all succeeding paths. Hence, it will circulate on ever widening semi-circles from the interior of one electrode to the interior of the other, gaining an increment of energy on each crossing of the diametral region corresponding to the momentary potential difference between the electrodes. Thus if, as in the early experiments of Lawrence and Livingston,[1] high frequency oscillations having peak values of 4000 volts are applied to the electrodes and protons are caused to spiral around in the electrodes 150 times they will receive 300 increments of energy acquiring thereby a speed corresponding to 1.2 M.v. Intensities vary from 10 μa. to 200 μa. The resonance principle involves a magnetic analysis of ion masses and velocities; only ions having the same e/m can be accelerated. Deuterons and hydrogen molecule ions have approximately the same e/m but their mean free paths are quite different. At sufficient gas pressures the molecule ions will be absorbed leaving the deuterons alone to reach the collector. Variations in ion energies less than about 2 per cent of the total energy can usually be attained. The ion beam is caused to emerge tangentially from the accelerating chamber by suitable electrostatic deflecting fields. It emerges through a thin window and is observable as a bluish ionization glow whose length is determined by the density of the atmosphere. The energies of the cyclotrons can be stated approximately by the ranges of the ion beams in air. Lawrence himself has built a sequence of cyclotrons of increasing size, varying in beam energy from 80 kv. to 16 M.e.v. The beam from this latter extends 60 inches through the air after leaving the chamber. Throughout the world, some thirty-five cyclotrons of varying sizes have been built. The majority of these can produce deuterons of 5 to 10 M.e.v. and currents of 10 to 200 μa. A new giant cyclotron whose beam, it is expected, will range in voltage from 100 to 300 M.v. is under construction in Berkeley. This beam may be expected to penetrate 140 feet of air.

(57) **The Results of Disintegration Experiments:** The number of disintegrations already achieved with α-particles from natural radioactive sources and with the high-speed ions, neutrons and gamma-rays has become so large that it has been found necessary to subdivide them into type-reactions and to devise a shorthand notation descriptive of each. There are used as projectiles, and appear as disintegration products, alpha-particles, protons, deuterons, neutrons and gamma-rays. To these are assigned respectively the symbols α, p, d, n and γ. The reactions produced by a given projectile and yielding a given product are designated by the corresponding symbols in order. Thus, α-particle disintegrations yielding protons are designated as reactions of the α–p type. A neutron bombardment which yields an α-particle would be symbolized as n–α. If such a designation is preceded by the chemical symbol of the substance bombarded the reaction occurring is completely specified. Thus ^{6}Li, n–α would designate the reaction ${}_3^6\text{Li} + {}_0^1 n = {}_1^3\text{H} + {}_2^4\text{He}$, since, from the required balance of charge and mass, the other disintegration product must be a hydrogen isotope and of mass 3. More generally, the nuclear charge may

---

[1] E. O. Lawrence and M. S. Livingston, *Phys. Rev.*, **40**, 19 (1932).

be designated as Z, the atomic number as A and the type reaction then becomes, for example, in an $\alpha-p$ reaction: $^{A}Z + {}^{4}He = {}^{A+4}(Z+2) = {}^{A+3}(Z+1) + {}^{1}H$. In Table XIV are listed the various type reactions that have been secured by such nuclear disintegrations.

TABLE XIV

TYPE-REACTIONS IN NUCLEAR TRANSFORMATIONS

Number	Shorthand Notation	Nuclear Reaction
1	$\alpha-p$	$^{A}Z + {}^{4}He = {}^{A+4}(Z+2) = {}^{A+3}(Z+1) + {}^{1}H$
2	$\alpha-n$	$^{A}Z + {}^{4}He = {}^{A+4}(Z+2) = {}^{A+3}(Z+2) + {}^{1}n$
3	$\alpha-2n$	$^{A}Z + {}^{4}He = {}^{A+4}(Z+2) = {}^{A+2}(Z+2) + 2^{1}n$
4	$p-\alpha$	$^{A}Z + {}^{1}H = {}^{A+1}(Z+1) = {}^{A-3}(Z-1) + {}^{4}He$
5	$p-d$	$^{A}Z + {}^{1}H = {}^{A+1}(Z+1) = {}^{A-1}Z + {}^{2}H$
6	$p-\gamma$	$^{A}Z + {}^{1}H = {}^{A+1}(Z+1) = {}^{A+1}(Z+1) + \gamma$
7	$p-n$	$^{A}Z + {}^{1}H = {}^{A+1}(Z+1) = {}^{A}(Z+1) + {}^{1}n$
8	$d-\alpha$	$^{A}Z + {}^{2}H = {}^{A+2}(Z+1) = {}^{A-2}(Z-1) + {}^{4}He$
9	$d-p$	$^{A}Z + {}^{2}H = {}^{A+2}(Z+1) = {}^{A+1}Z + {}^{1}H$
10	$d-p, \alpha$	$^{A}Z + {}^{2}H = {}^{A+2}(Z+1) = {}^{A-3}(Z-2) + {}^{1}H + {}^{4}He$
11	$d-n$	$^{A}Z + {}^{2}H = {}^{A+2}(Z+1) = {}^{A+1}(Z+1) + {}^{1}n$
12	$d-n, \alpha$	$^{A}Z + {}^{2}H = {}^{A+2}(Z+1) = {}^{A-3}(Z-1) + {}^{1}n + {}^{4}He$
13	$d-2n$	$^{A}Z + {}^{2}H = {}^{A+2}(Z+1) = {}^{A}(Z+1) + 2^{1}n$
14	$n-\alpha$	$^{A}Z + {}^{1}n = {}^{A+1}Z = {}^{A-3}(Z-2) + {}^{4}He$
15	$n-p$	$^{A}Z + {}^{1}n = {}^{A+1}Z = {}^{A}(Z-1) + {}^{1}H$
16	$n-\gamma$	$^{A}Z + {}^{1}n = {}^{A+1}Z = {}^{A+1}Z + \gamma$
17	$n-2n$	$^{A}Z + {}^{1}n = {}^{A+1}Z = {}^{A-1}Z + 2^{1}n$
18	$\gamma-n$	$^{A}Z + \gamma = {}^{A}Z = {}^{A-1}Z + {}^{1}n$

À $p-2n$ reaction is to be expected at high energies. The $\alpha-\gamma$ reaction has not yet been observed but is to be expected at an energy below the $\alpha-n$ threshold. There appears, also, to be an additional type of nuclear transformation with deuterons as bombarding agent and radioactive hydrogen, tritium (^{3}H, t), as the expelled particle. This type of reaction has been found [1,2] for $^{9}Be(d, t){}^{8}Be$ and $^{14}N(d, t){}^{13}N$ with indications [3] of similar reactions in ^{63}Cu and ^{107}Ag.

We can generalize the product in the final column of this table by the general formula $^{A \pm x}(Z \pm y)$ where x varies from $+3$ to -3 and y varies from $+2$ to -2 depending on the nature of the emitted particle or radiation. If the product $^{A \pm x}(Z \pm y)$ corresponds with one of the stable isotopes the nuclear transformation is complete. A list of such stable isotopes and their relative abundances is shown in Table XV in which are included, also, the more abundant naturally occurring radioelements, indicated by an asterisk. The table includes 277 stable isotopes and 9 of the naturally occurring radioelements.

The products of these nuclear transformations, of the general formula $^{A \pm x}(Z \pm y)$, are not always stable nuclei. In some three hundred and fifty cases already known the product is not stable but undergoes further radioactive

[1] R. D. O'Neal and M. Goldhaber, *Phys. Rev.*, **57**, 1086A (1940).

[2] L. B. Borst, *ibid.*, **59**, 941A (1941).

[3] Krishman and Gant, *Nature*, **144**, 547 (1939); Krishman and Banks, *ibid.*, **145**, 777 (1940).

TABLE XV

Stable Isotopes of the Elements and Their Abundances [1]

Element	Atomic Weight	Per Cent Abundance	Element	Atomic Weight	Per Cent Abundance	Element	Atomic Weight	Per Cent Abundance
₁H	1	99.98	₂₁Sc	45	100	₃₆Kr	78	0.35
	2	0.02	₂₂Ti	46	7.95		80	2.01
₂He	3	~10⁻⁴		47	7.75		82	11.53
	4	100		48	73.45		83	11.53
₃Li	6	7.9		49	5.51		84	57.10
	7	92.1		50	5.34		86	17.47
₄Be	9	100	₂₃V	51	100	₃₇Rb	85	72.3
₅B	10	18.4	₂₄Cr	50	4.49		87*	27.7
	11	81.6		52	83.77	₃₈Sr	84	0.56
₆C	12	98.9		53	9.43		86	9.86
	13	1.1		54	2.30		87	7.02
₇N	14	99.62	₂₅Mn	55	100		88	82.56
	15	0.38	₂₆Fe	54	6.04	₃₉Y	89	100
₈O	16	99.76		56	91.57	₄₀Zr	90	48
	17	0.04		57	2.11		91	11.5
	18	0.20		58	0.28		92	22
₉F	19	100	₂₇Co	57	0.17		94	17
₁₀Ne	20	90.00		59	99.83		96	1.5
	21	0.27	₂₈Ni	58	67.4	₄₁Cb	93	100
	22	9.73		60	26.7	₄₂Mo	92	15.5
₁₁Na	23	100		61	1.2		94	8.7
₁₂Mg	24	77.4		62	3.8		95	16.3
	25	11.5		64	0.9		96	16.8
	26	11.1	₂₉Cu	63	68		97	8.7
₁₃Al	27	100		65	32		98	25.4
₁₄Si	28	89.6	₃₀Zn	64	50.9		100	8.6
	29	6.2		66	27.3	₄₄Ru	96	5
	30	4.2		67	3.9		98	?
₁₅P	31	100		68	17.4		99	12
₁₆S	32	95.0		70	0.5		100	14
	33	0.74	₃₁Ga	69	61.2		101	22
	34	4.2		71	38.8		102	30
	36	0.016	₃₂Ge	70	21.2		104	17
₁₇Cl	35	75.4		72	27.3	₄₅Rh	101	0.08
	37	24.6		73	7.9		103	99.92
₁₈A	36	0.307		74	37.1	₄₆Pd	102	0.8
	38	0.061		76	6.5		104	9.3
	40	99.632	₃₃As	75	100		105	22.6
₁₉K	39	93.3	₃₄Se	74	0.9		106	27.2
	40*	0.012		⁻76	9.5		108	26.8
	41	6.7		77	8.3		110	13.5
₂₀Ca	40	96.96		78	24.0	₄₇Ag	107	52.5
	42	0.64		80	48.0		109	47.5
	43	0.15		82	9.3	₄₈Cd	106	1.4
	46	0.0$_2$33	₃₅Br	79	50.6		108	1.0
	48	0.19		81	49.4		110	12.8

[1] Based on the table of Livingood and Seaborg, *Rev. Mod. Phys.*, **12**, 30 (1940).
* Indicates natural radioactivity.

TABLE XV—*Continued*

| Element	Atomic Weight	Per Cent Abundance	Element	Atomic Weight	Per Cent Abundance	Element	Atomic Weight	Per Cent Abundance
48Cd	111	13.0	58Ce	142	10	72Hf	172(?)	<0.1
	112	24.2	59Pr	141	100		174	0.3
	113	12.3	60Nd	142	25.95		176	5.0
	114	28.0		143	13.0		177	19
	116	7.3		144	22.6		178	28
49In	113	4.5		145	9.2		179	18
	115	95.5		146	16.5		180	30
50Sn	112	1.1		148	6.8	73Ta	181	100
	114	0.8		150	5.95	74W	180	~0.2
	115	0.4	62Sm	144	3		182	22.6
	116	15.5		147	17		183	17.3
	117	9.1		148*	14		184	30.1
	118	22.5		149	15		186	29.8
	119	9.8		150	5	75Re	185	38.2
	120	28.5		152	26		187	61.8
	122	5.5		154	20	76Os	184	0.018
	124	6.8	63Eu	151	49.1		186	1.59
51Sb	121	56		153	50.9		187	1.64
	123	44	64Gd	152	0.2		188	13.3
52Te	120	<0.1		154	1.5		189	16.1
	122	2.9		155	20.7		190	26.4
	123	1.6		156	22.6		192	41.0
	124	4.5		157	16.7	77Ir	191	38.5
	125	6.0		158	22.6		193	61.5
	126	19.0		160	15.7	78Pt	192	0.8
	128	32.8	65Tb	159	100		194	30.2
	130	33.1	66Dy	158	0.1		195	35.3
53I	127	100		160	1.5		196	26.6
54Xe	124	0.094		161	21.6		198	7.2
	126	0.088		162	24.6	79Au	197	100
	128	1.90		163	24.6	80Hg	196	0.15
	129	26.23		164	27.6		198	10.1
	130	4.07	67Ho	165	100		199	17.0
	131	21.17	68Er	162	0.25		200	23.3
	132	26.96		164	2.0		201	13.2
	134	10.54		166	35.2		202	29.6
	136	8.95		167	23.5		204	6.7
55Cs	133	100		168	29.3	81Tl	203	29.1
56Ba	130	0.101		170	9.8		205	70.9
	132	0.097	69Tm	169	100	82Pb	204	1.48
	134	2.42	70Yb	168	0.06		206	23.59
	135	6.59		170	2		207	22.64
	136	7.81		171	8.8		208	52.29
	137	11.32		172	23.5	83Bi	209	100
	138	71.66		173	16.7	90Th	232*	100
57La	139	100		174	37.2	91Pa	231*	
58Ce	136	<1		176	11.8	92U	234*	0.006
	138	<1	71Lu	175	97.5		235*	0.71
	140	90		176*	2.5		238*	99.28

change as was first pointed out by Curie and Joliot [1] early in 1934. With their observation the study of induced radioactivity was begun.

(58) **Products of Induced Radioactivity:** The data in Column 2 of Table XVI reveal that the principal types of radiation from induced radioactive elements are negative β-particles, (β^-), positive β-particles or positrons, (β^+) and γ-rays. Internal-conversion electrons, e^-, may be formed and K-electron capture also occurs. In this case, nuclear stability is achieved by capture of an extra-nuclear electron, normally from the K-shell. Radioactive nuclei also exist in isomeric states and isomeric transitions (I.T.) are also found. Thus, ^{69}Zn with a half-life of 13.8 hr. undergoes an isomeric transition to a radioactive isomer ^{69}Zn with emission of γ-radiation to the amount of 0.47 M.e.v. The ^{69}Zn isomer in the lower energy state has a half-life of 57 min. and emits a negative β-particle (β^-) with an energy of 1 M.e.v. but no gamma-radiation. Both isomers are produced by the same bombardment processes as the data of Table XVI indicate. The table also includes the products of nuclear fission (see Section 63). The reactions are designated by the symbols U, n; Th, n and Pa, n respectively in the fifth column of the table. The fission product is the radioelement listed in the corresponding line of the first column of the table. A second or later unit in a sequence of products from a nuclear fission is listed as produced by the beta-decay of its immediate parent isotope.

(59) **Positron-Production from Nuclear Disintegration:** In January 1934 Irène Curie and F. Joliot [2] announced that α-particle bombardment from polonium sources of boron, magnesium or aluminum produced artificial or induced radioactivity, that the radioactive rays emitted consisted of positrons, the half-lives of the radioactive materials being characteristic of each species bombarded. Thus, with aluminum, a half-life period of 2.55 min. was observed, now known to be due to a sequence of two processes, the first yielding a neutron and radio-phosphorus,

$$^{27}_{13}\text{Al} + {}^4_2\text{He} = {}^1_0n + {}^{30}_{15}\text{P},$$
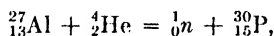
the latter disintegrating to a silicon isotope with positron emission

$$^{30}_{15}\text{P} = {}^{30}_{14}\text{Si} + \beta^+.$$
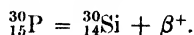
This sequence of processes constituted about 5 per cent of the total of nuclear change involved in the interaction of aluminum and α-particles since the direct reaction to yield the same silicon and a proton occurs twenty times as often

$$^{27}_{13}\text{Al} + {}^4_2\text{He} = {}^{30}_{14}\text{Si} + {}^1_1\text{H}.$$
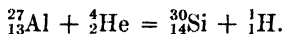
The positron activity was then reported from other elements such as nitrogen, fluorine, sodium, phosphorus and potassium. The same reaction sequence occurs as in the case of aluminum just cited. Also, other bombarding agents

[1] I. Curie and F. Joliot, *ibid.*, **133**, 201 (1934).

[2] I. Curie and F. Joliot, *Compt. rend.*, **198**, 254, (1934); *J. phys. Radium*, **5**, 153 (1934).

TABLE XVI

INDUCED RADIOACTIVITIES [1]

Radio-element	Type of Radiation	Half-Life	Energy of Radiation M.e.v.	Method of Production
^{3}H	β^-	>10y.	~0.013	D, d–p ; Be, d–^{3}H
^{6}He	β^-	0.8s.	3.7	Be, n–α ; (Li, n–p) ; Li, d–p ; B, n–α
^{8}Li	β^-, α	0.88s.	12(β^-)	(Li, n–γ) ; Li, d–n ; B, p–α ; Li, p–n ; Be, d–p
^{7}Be	K, γ	53d.	0.45(γ)	
^{10}Be	β^-, γ	≫10^{6}y.	0.5(β^-) <0.5(γ)	B, d–p ; B, p–n ; B, d–n
^{12}B	β^-	0.022s.	12	B, p–γ ; B, p–n ; N, p–α ; C, n–$2n$
^{10}C	β^-	8.8s.	3.4	
^{11}C	β^+	20.5m.	0.95	C, d–p ; N, n–p ; C, d–n
^{14}C	β^-	≫10^{3}y.	0.090	
^{13}N	β^+, γ	9.93m.	0.92(β^+)	
^{13}N	β^+, γ	9.93m.	1.20(β^+) 0.28(γ)	C, p–γ ; B, α–n ; N, n–$2n$; N, d–p ; O, n–p ; F, n–α
^{16}N	β^-	8s.	6.0	N, d–α ; O, γ–n ; O, n–$2n$; N, p–γ
^{15}O	β^+	2.1m.	1.7	C, α–n ; F, n–p ; O, d–n ; N, α–n ; O, p–γ
^{19}O	β^-	31s.		Ne, d–α ; O, p–n ; F, n–$2n$; O, d–n
^{17}F	β^+	70s.	2.1	
^{19}F	β^+	112m.	0.7	
^{20}F	β^-, γ	12s.	5.0(β) 2.2(γ)	F, d–p ; F, n–γ ; Na, n–α

[1] Based on the tables of Livingood and Seaborg, *Rev. Mod. Phys.*, 12, 30 (1940) and Seaborg, *Chem. Rev.*, 27, 225 (1940) with additions from the American literature up to May 30, 1941.

Column 2 lists the types of radiation: β^- = negative beta-particles (electrons), β^+ = positive beta-particles (positrons), γ = gamma rays, e^- = internal conversion electrons, K = K-electron capture, I.T. = isomeric transition, from upper to lower isomeric state. Annihilation gamma-rays from positron annihilation are not listed. The half-lives in Column 3 are given in seconds (s.), minutes (m.), hours (h.), days (d.) and years (y.).

* Radioactive isomer of stable nucleus.

TABLE XVI—Continued

Radio-element	Type of Radiation	Half-Life	Energy of Radiation M.e.v.	Method of Production
¹⁹Ne	β^+	20.3s.	2.2	F, p–n
²³Ne	β^-	40s.	4.1	Na, n–p
				Mg, n–α
²¹Na		28s.		Ne, d–p
				Ne, p–n
²²Na	β^+	3y.	0.58(β^+)	Ne, d–n
			1.3(γ)	Mg, d–α
				F, α–n
²⁴Na	β^-, γ	14.8h.	1.4(β^-)	Ne, d–n
			1.46(γ)	Na, n–γ
			2.0(γ)	Na, d–p
			3.03(γ)	Mg, n–p
				Al, n–α
²³Mg	β^+	11.6s.	2.82	Mg, d–α
²⁷Mg	β^-, γ	10.2m.	1.8(β^-)	Na, p–n
			0.9(γ)	Mg, d–p
				Mg, n–γ
				Al, n–p
²⁶Al	β^+	7.0s.	2.99	Na, α–n
				Mg, p–n
				Mg, p–γ
²⁸Al	β^-, γ	2.4m.	3.3(β^-)	Al, d–p
			2.3(γ)	Al, n–γ
				Si, n–p
				P, n–α
²⁹Al	β^-	6.7m.	2.5	Mg, α–p
²⁷Si	β^+	4.92s.	3.74	Mg, α–n
				Al, p–n
				Mg, α–n
³¹Si	β^-	2.83h.	1.8	Si, d–p
³¹Si	β^-	2.83h.	1.8	Si, n–γ
				P, n–p
				S, n–α
²⁹P	β^+	<10s.		Si, p–n
³⁰P	β^+	2.55m.	3.0	Al, α–n
				S, d–α
				P, n–$2n$
				P, γ–n
				Si, p–n
				Si, ³He–p
³²P	β^-	14.3d.	1.69	P, α–p
				P, n–γ
				S, n–p
				Cl, n–α
³¹S	β^+	3.18s.	3.85	S, d–α
				Si, α–p
				P, p–n
				Si, α–n
³⁵S	β^-	88d.	0.107	Cl, n–p
				S, d–p
³³Cl	β^-	2.8s.		S, α–n
³⁴Cl	β^+	33m.	2.5	P, α–n
				S, d–n
				Cl, n–$2n$
				Cl, γ–n
³⁶Cl	β^+, K, β^-	>1y.	0.7(β^-)	S, α–p, n
				S, α–d
³⁸Cl	β^-, γ	37m.	1.1, 5.0(β^-)	Cl, n–γ
				Cl, d–p
				Cl, d–p

95

TABLE XVI—Continued

Radio-element	Type of Radiation	Half-Life	Energy of Radiation M.e.v.	Method of Production
^{38}Cl	β^-, γ	37m.	1.65, 2.15(γ)	Cl, n-γ; K, n-α
^{35}A	β^+	1.88s.	4.4	S, α-n
^{39}A	β^-	4m.		K, n-p
^{41}A	β^-, γ	110m.	1.5(β^-), 1.37(γ)	A, d-p; K, n-p
^{38}K	β^+, γ	7.7m.	2.3(β^-)	A, n-γ; Cl, α-n; Ca, d-α
^{42}K	β^-	12.4h.	3.5	K, n-$2n$; K, d-p; K, n-γ; Ca, n-p; Sc, n-α
^{43,44}K	β^-	18m.		Ca, n-p; Ca, n-$2n$(?)
^{39}Ca	β^+	4.5m.	1.1(γ)	Ca, d-p
^{41}Ca	K, γ, e^-	8.5d.		Ca, n-$2n$
^{45}Ca	β^-, γ	180d.	0.2, 0.9(β^-), 0.7γ	Ca, n-γ; Ca, d-p; Se, n-p
^{49}Ca	β^-, γ	2.5h.	2.3(β^-), 0.8(γ)	Ca, d-p; Ca, n-γ
^{41}Sc	β^+	0.87s.	4.94	Ca, d-n; K, α-n
^{42}Sc	β^+	13.5d.	1.4	Ca, α-p; Ca, d-n
^{43}Sc	β^+	4h.	0.4, 1.4(β^-), 1.0γ	Ca, p-n; Ca, d-n
^{44}Sc	I.T., e^-, γ	52h	0.26(γ)	Sc, n-$2n$; K, α-n

Radio-element	Type of Radiation	Half-Life	Energy of Radiation M.e.v.	Method of Production
^{44}Sc	I.T., γ^-, γ	52h.	0.26(γ)	Ca, d-n; Ca, p-n; Ti, d-α; Sc, n-$2n$
^{44}Sc	β^-	4.1h.	1.5	K, α-n; Ca, d-n; Ca, d-n; Sc, γ-n; ^{44}Sc, (52h.)
^{45}Sc	β^-, γ, K	85d.	0.26, 1.5(β^-), 1.25(γ)	Sc, d-p; Sc, n-γ; Ti, d-α
^{46}Sc	β^-, γ	63h.	1.1(β^-)	Ti, n-p; Ca, α-p; Ti, n-p
^{48}Sc	β^-, γ	44h.	0.5, 1.4(β^-), 0.9(γ)	Ti, n-p; V, n-α
^{49}Sc	β^-	57m.	1.8	Ca, d-n; ^{49}Ca, (2.5h.)
^{51}Ti	β^-, γ	2.9m.		Ti, n-p; Ti, d-p
^{51}Ti	β^-, γ	72d.	0.36(β^-), 1.0(γ)	Ti, n-γ; Ti, d-p; Ti, n-γ
^{47}V	K	600d.	1.0(β^-)	Ti, d-n; Ti, d-n
^{48}V	β^-, K, γ	16d.	1.05(γ)	Sc, α-n; Cr, d-α; Ti, p-n

TABLE XVI—Continued

Radio-element	Type of Radiation	Half-Life	Energy of Radiation M.e.v.	Method of Production
⁴⁹V	β⁺	33m.	1.9	Ti, d–n; Ti, α–p
⁵⁰V	β⁺	3.7h.		Ti, p–n; V, n–2n
⁵²V	β⁻	~3.9m.	2.05	Ti, d–n; Ti, α–p; V, n–γ; V, d–p; Cr, n–p; Mn, n–α
⁵¹Cr	K, γ, e⁻	26.5d.	0.5, 1(γ)	Ti, α–n; Cr, α–p; Cr, n–γ; Cr, n–2n; Cr, n–γ; Cr, d–p; Cr, d–n; Cr, p–γ; Fe, d–α
⁵⁵Cr		1.6–2.3h.		Cr, p–n; Fe, d–α; Fe, d–α
⁵¹Mn	β⁺	46m.	2.0	
⁵²Mn	β⁺, γ	21m.	2.2(β⁺); 1.2(γ)	
⁵³Mn	β⁺, γ, K	6.5d.	0.77(β⁻); 1.0(γ)	
⁵⁴Mn	K, γ	310d.	0.85(γ)	Cr, p–n; Mn, n–γ; Mn, d–p; Fe, d–α; Fe, n–p
⁵⁶Mn	β⁻, γ	2.5h.	1.2, 2.9(β⁻); 0.7, 1.7(γ)	
⁵⁶Mn	β⁻, γ	2.5h.	0.7, 1.7(γ)	Co, n–α; Cr, α–p; Cr, α–n
⁵³Fe	β⁺	8.9m.		Fe, n–2n
⁵⁵Fe	K, e⁻	~4y.		Fe, d–p; Mn, p–n
⁵⁹Fe	β⁻, γ	47d.	0.4, 0.9(β⁻); 1.0(γ)	Fe, d–p; Co, n–p; Fe, d–n; Fe, p–γ
⁵⁵Co	β⁺, γ	18.2h.	1.50(β⁺); 0.16, 0.21; 0.8, 1.2(γ)	
⁵⁶Co	K, γ, e⁻	270d.	0.4(β⁻)	Fe, d–2n; Ni, d–α; Fe, p–n; Fe, d–n; Mn, α–n; Ni, d–α; Fe, p–n
⁵⁸Co	β⁺, γ	72d.	<0.5(β⁻); 0.6(γ)	Ni, n–p; Co, d–p.; Co, n–γ; Co, n–γ
⁶⁰Co	β⁻, γ	5.5y.	0.16, 1.5(β⁻); 1.3(γ)	Ni, n–p
⁶⁰Co	I.T.(?), e⁻	11m.		Fe, α–n
⁵⁷Ni	β⁺	36h.	0.67	Ni, n–2n(?); Ni, d–p
⁶³Ni	β⁻, γ	2.6h.	1.9(β⁻); 1.1(γ)	Ni, n–γ; Cu, n–p; Zn, n–α; Ni, n–2n

97

TABLE XVI—*Continued*

Radio-element	Type of Radiation	Half-Life	Energy of Radiation M.e.v.	Method of Production
⁵⁸,⁶⁰Cu	β⁺	81s.		Ni, p-n
⁵⁸,⁶⁰Cu	β⁺	7.9m.		Ni, p-n
⁶¹Cu	β⁺, K	3.4h.	0.9	Ni, d-n; Ni, p-n; Ni, p-γ
⁶²Cu	β⁺	10.5m.	2.6	Ni, α-p; Cu, n-2n; Cu, γ-n; Co, α-n; Ni, p-n; Ni, p-γ
⁶⁴Cu	β⁻, β⁺, K	12.8h.	0.58(β⁻) 0.66(β⁺)	Cu, d-p, 2n; Cu, d-p; Cu, n-γ; Cu, n-2n
⁶⁶Cu	β⁻	5m.	2.9	Ni, p-n; Zn, n-p; Cu, n-γ
⁶⁸Cu	β⁺	38m.	2.3	Ga, n-α; Cu, d-p; Zn, n-2n; Zn, γ-n; Cu, p-n
⁶⁵Zn	β⁺, K, γ; e⁻	250d.	0.4(β⁺) 0.45, 0.65 1.0(γ)	Ni, α-n; Cu, d-2n; Zn, d-p; Cu, d-2n; Cu, p-n; Zn, n-γ
⁶⁵Zn	e⁻; I.T., γ	250d.; 13.8h.	1.0(γ); 0.47(γ)	⁶⁵Ga, K decay; Zn, d-p
⁶⁹Zn	β⁻	57m.	1.0	Zn, n-γ; Ga, d-α; Ga, n-p; Zn, d-p; Zn, n-γ; Ga, d-α; Ga, d-α; ⁶⁹Zn, (I.T.)
⁶⁴Ga	β⁺	48m.		Zn, p-n
⁶⁵Ga	K, e⁻	15m.	0.054, 0.117(γ)	Zn, d-n
⁶⁶Ga	β⁺	9.4h.	3.1	Zn, p-γ; Cu, α-n; Zn, p-n
⁶⁷Ga	K, γ, e⁻	83h.	0.0925 0.18, 0.30	Zn, d-n; Zn, α-p; Zn, p-n
⁶⁸Ga	β⁺	68m.	1.9	Zn, α-p; Zn, p-n; Cu, α-n; Ga, n-2n; Ga, γ-n; Zn, p-n; Zn, p-γ(?); Zn, d-n
⁷⁰Ga	β⁻, γ	20m.	1.7(β⁻)	Ga, n-γ; Ga, n-2n; Ga, γ-n; Zn, p-n
⁷²Ga	β⁻, γ	14h.	2.6(β⁻)	Zn, α-p; Ga, d-p

TABLE XVI—Continued

Radio-element	Type of Radiation	Half-Life	Energy of Radiation M.e.v.	Method of Production
^{7}Ga	β^-,γ	14h.	1.0(γ)	Ga, $n-\gamma$
^{69}Ge(?)	β^+	29m.	0.6	Ge, $n-2n$
^{7}Ge	K, e^-	11d.		Ge, $n-?$
^{71}Ge	β^+	40h.	1.0	Ge, $d-2n$; Zn, $\alpha-n$; Ge, $n-\gamma$; Ge, $d-p$; Ga, $d-2n$; Ge, $n-2n$
^{67,69,71}Ge				Zn, $\alpha-n$; Ge, $n-\gamma$; Ge, $d-p$
^{75}Ge	β^-	195d.	1.1	As, $n-p$; Ge, $n-2n$
^{77}Ge	β^-	89m.	1.9	Ge, $n-\gamma$; Ge, $d-p$; Se, $n-\alpha$
^{71}As	β^+,γ	12h.		Ge, $d-n$
^{71}As	β^+,γ	50h.		Ge, $d-n$
^{72}As	β^+	88m.		Ge, $p-n$
^{74}As	β^-,β^+,γ	24h.	1.3(β^-); 0.9(β^+)	As, $n-2n$; Ge, $d-n$; Se, $d-n$
^{76}As	β^-,γ; β^+,K	16d.; 26.8h.	1.1, 1.7, 2.7(β^-); 0.7, 2.6(β^+); 3.2, 2.2, 1.5(γ)	Ge, $p-n$; As, $d-p$; As, $n-\gamma$; Br, $n-\alpha$; Se, $n-p$; Se, $d-\alpha$

Radio-element	Type of Radiation	Half-Life	Energy of Radiation M.e.v.	Method of Production
^{77}As	β^-,γ	90d.	0.12(β^-)	Ge, $d-n$; Br, $n-\alpha$; Se, $n-p$; As, $p-n$
^{78}As	β^-,γ	65m.	1.4(β^-)	Se, $d-p$; Se, $n-\gamma$; Br, $n-p$
^{75}Se	K,γ,e^-	48d.	0.27(γ)	Se, $\gamma-n$; Se, $\gamma-n$; Se, $d-p$; Se, $n-\gamma$
^{79,81}Se	I.T., e^-	57m.	0.50(γ); 0.098(γ)	Se, $\gamma-n$; Br, $n-p$; ^{79,81}Se, (57m.)
^{79,81}Se	β^-	19m.	1.5	Se, $d-p$; Se, $n-\gamma$
^{83}Se	β^-	30m.		Th, n
Se		>1h.		Th, n
Se		>1d.		Se, $d-n$
^{79}Br	β^+, e^-,γ	6.4m.	2.3(β^+); 0.046, 0.108(γ)	As, $\alpha-n$; Br, $\gamma-n$; Br, $n-2n$; Se, $n-\gamma$
^{80}Br	I.T., e^-; γ	4.4h.	0.049; 0.037 or 0.025(γ)	Br, $n-\gamma$; Br, $d-p$; Se, $p-n$; Br, $\gamma-n$; Br, $n-2n$
^{80}Br	β^+,γ	18m.	2.0(β^+); <0.5(γ)	Br, $d-p$; Br, $d-p$; Se, $p-n$

99

TABLE XVI—*Continued*

Radio-element	Type of Radiation	Half-Life	Energy of Radiation M.e.v.	Method of Production
^{80}Br	β^+, γ	18m.	2.0(β^+) <0.5(γ)	Br, γ-n Br, n-$2n$
^{82}Br	β^-, γ	34h.	0.7(β^-) 0.65(γ)	^{80}Br, (4.4h.) Br, n-γ Br, d-p
^{83}Br	β^-	140m.	1.05	Se, $p{\to}n$ Se, d-n Rh, n-α Se, d-n ^{83}Se, β^- decay
>^{82}Br		40m.		Th, n U, n
>^{82}Br		22h.		U, n
>^{83}Br		3.8h.		Th, n U, n
^{79,81}Kr	β^+	34h.	0.5	Kr, d-p Br, p-n Se, α-n Br, p-n
^{79,81}Kr	I.T.(?) e^- γ	13s.	0.187(γ)	Br, p-n
^{79,81}Kr	I.T.(?), e^- γ	55s.	0.127(γ)	Br, p-n Se, α-n(?)
^{83}Kr*	I.T., e^-	113m.	0.049(γ)	^{83}Br, β^- decay Se, α-n Kr, d-p Kr, d-p Se, α-n(?) Kr, d-p
^{87}Kr	β^-	74m.		Th, n U, n
^{88}Kr	β^-	4.5h.		
^{88}Kr	β^-	3h.		
^{89}Kr	β^-	~2m.		

Radio-element	Type of Radiation	Half-Life	Energy of Radiation M.e.v.	Method of Production
>^{90}Kr	β^-	<0.5m.		Th, n U, n
^{82}Rb		20m.		Br, α-n Br, α-n
^{84}Rb		6.5h.		Kr, d-n Kr, d-n Kr, d-n
Rb		42m.		Rb, n-γ Pa, n
Rb		200h.		
^{88}Rb	β^-	18m.	4.6	^{88}Kr, β^- decay ^{89}Kr, β^- decay
^{89}Rb	β^-, γ	15m.	3.8(β^-)	Rb, n-γ
^{90}Rb	β^-	18–19.5d.	1.56	Sr, d-α
>^{90}Rb	β^-	80s.	0.8(γ)	>^{90}Kr, β^- decay Rb, p-n
^{85}Sr	K, γ	65d.	0.17(γ)	Rb, p-n Sr, n-n
^{85}Sr	I.T., e^-, γ	70m.	0.37(γ)	Rb, p-n
^{87}Sr*	I.T., e^-, γ	2.7h.		Sr, d-p Sr, n-γ
^{89}Sr	β^-	55d.	1.50	^{87}Y, 80h. K decay Sr, p-p(?) Zr, n-α Sr, d-p Sr, n-γ Y, n-p
>^{90}Sr	β^-	7m.		^{89}Rb, β^- decay Zr, n-α(?) U, n
>^{90}Sr	β^-	6h.		>^{90}Rb, β^- decay

100

TABLE XVI—Continued

Radio-element	Type of Radiation	Half-Life	Energy of Radiation M.e.v.	Method of Production
^{86}Y	K, γ	105d.	0.95, 1.92	Sr, p-n
^{87}Y	I.T., e^-, γ	14h.	0.5(γ)	Sr, d-n
^{87}Y	K	80h.		Sr, p-n; Sr, d-n
^{88}Y	β^+	2h.	1.2	Sr, p-n; Sr, d-n; Y, n-2n
^{90}Y	β^-	60h.	2.6	Y, d-p; Y, n-γ; Cb, n-α; Zr, n-p; Zr, d-α
>^{90}Y		3.3h.	1.0	>^{90}Sr, 6h. β^- decay; Zr, n-p; Zr, n-2n; Y, n-p
^{89}Zr	β^+	78h.		Mo, n-α; Y, p-n
^{89}Zr	e^-; γ; I.T. or K	4.5m.		Zr, n-γ
Zr	β^-	18m.		Zr, d-?
Zr	β^-	90m.		Zr, n-?
Zr	β^-	70h.	1.17	Zr, n-γ
^{93}Zr	β^-	63d.	~0.25	Zr, d-p; Mo, n-α(?)
^{95}Zr	β^-	17h.	1	U, n; Zr, n-γ; Mo, n-α
^{97}Zr	β^-	6m.	~1.9	Zr, n-γ
Zr	β^-	>20d.	~0.25	U, n
Cb		4m.		Zr, p-n(?)
Cb		12m.		Zr, p-n(?)
Cb		38m.		Zr, p-n(?)
Cb		21h.		Zr, p-n(?)
Cb		96h.		Zr, p-n(?)
^{92}Cb	β^-	11d.	1.38	Cb, n-2n; Mo, n-p
^{93}Cb*	I.T., e^-	~55d.	~0.15(e^-)	^{93}Zr, β^- decay
^{94}Cb	β^-, γ	6.6m.	1.4(β^-), 0.4(γ)	Cb, n-γ
^{95}Cb	β^-	75m.	1	^{95}Zr, β^- decay; Mo, n-p
^{99}Mo	β^-	7h.		Cb, p-n(?); Mo, n-2n
$^{91, 93}$Mo	β^-	17m.	2.65	Mo, γ-n
^{99}Mo	β^-, γ	67h.	1.5(β^-), 0.4(γ)	Mo, d-p; Mo, n-γ; U, n; Th. n
^{101}Mo	β^-	19m.	1.8	Mo, n-2n; Mo, n-γ
^{99}43	β^-(?)	2.7h.		Cb, α-n; Mo, p-n; Mo, d-n
^{99}43	I.T., e^-, γ	6.6h.	0.136(γ)	^{99}Mo, β^- decay
^{101}43	β^-	9m.	1.1	^{101}Mo, β^- decay
43	K, e^-	90d.	0.096	Mo, d-n

101

TABLE XVI—Continued

Radio-element	Type of Radiation	Half-Life	Energy of Radiation M.e.v.	Method of Production
43	K, γ	62d.		Mo, d-n
43	$K(?), e^-, \gamma$	110h.	$0.6(e^-)$ 0.05, $0.5(\gamma)$	Mo, p-n
43	β^-, γ	55m.	$2.5(\beta^-)$	Mo, p-n
43	β^-	36.5h.		Mo, p-n
43	β^-	18s.		Mo, d-n
43	K	~2d.		Ru, n-$2n(?)$
⁹⁹Ru		20m.		Ru, n-γ
¹⁰³Ru	β^-	4h.		Ru, n-$2n$
				Ru, d-p
¹⁰⁵Ru	β^-	20h.		Ru, n-γ
Ru	β^-	39h.		Ru, d-?
Ru		11d.		Ru, d-?
Ru		90m.		Mo, α-n
¹⁰⁴Rh	I.T., e^-	4.2m.	0.055-$0.080(\gamma)$	Rh, n-γ
				Ru, p-n
¹⁰⁴Rh	β^-	44s.	2.3	Rh, n-γ
				¹⁰⁴Rh (I.T.)
				Ru, p-n
¹⁰⁶Rh	β^-	46d.		¹⁰⁶Ru, β^- decay
Rh		1.1h.		Ru, d-n
Rh		3h.		Rh, n-?
Rh		10.7h.		Ru, p-$n(?)$
Rh		3d.		Ru, p-$n(?)$
				Ru, p-$n(?)$
¹⁰⁷,¹⁰⁹Pd	β^-	13h.	1.03	Pd, d-p
				Pd, n-γ
¹¹¹Pd	β^-	17m.		Ag, n-p
				Pd, d-p

Radio-element	Type of Radiation	Half-Life	Energy of Radiation M.e.v.	Method of Production
¹¹¹Pd	β^-	17m.		Pd, n-γ
¹⁰²Ag		73m.		Pd, p-n
¹⁰⁴Ag	K	16.3m.		Pd, p-n
¹⁰⁵Ag		45d.	0.29, 0.42 0.50, 0.62	Pd, p-n
¹⁰⁶Ag	β^+	24.5m.	2.04	Ag, n-$2n$
				Pd, d-n
				Cd, n-p
				Rh, α-n
				Ag, γ-n
				Pd, p-γ
				Pd, p-n
¹⁰⁶Ag	$K(?), e^-, \gamma$	8.2d.	$1.2(e^-)$ 1.06, $0.69(\gamma)$	Ag, n-$2n$
				Pd, d-n
				Rh, α-n
				Pd, p-n
				Cd, n-p
¹⁰⁷,¹⁰⁹Ag	I.T., e^-	40s.	$0.093(\gamma)$	Ag, d-p, $2n(?)$
				¹⁰⁷,¹⁰⁹Cd, K decay 6.7h. and 158d.
				Ag, n-$2n$
¹⁰⁸Ag	β^-	2.3m.	2.8	Ag, n-γ
				Ag, γ-n
				Pd, p-n
				Cd, n-p
				Ag, d-p
¹¹⁰Ag	β^-, γ	22s.	$2.8(\beta^-)$	Ag, n-γ
				Cd, n-p
¹⁰⁸,¹¹⁰Ag	β^-	225d.		Ag, n-γ
				Ag, d-p

TABLE XVI—Continued

Left portion:

Radio-element	Type of Radiation	Half-Life	Energy of Radiation M.ev.	Method of Production
¹¹¹Ag	β⁻	7.5d.		Pd, d-n / Pd, α-p / Cd, n-p / ¹¹¹Pd, β⁻ decay
¹¹²Ag	β⁻, γ	3.2h.	2.2(β⁻)	Cd, n-p / In, n-α / U, n
¹⁰⁷,¹⁰⁹Cd	K, γ	6.7h.	0.53(γ)	Ag, p-n / Ag, d-2n
¹⁰⁷,¹⁰⁹Cd	K	158d.	0.6(γ)	Ag, d-2n / Cd, n-2n
¹⁰⁹Cd	β⁺	33m.		Cd, d-p
¹¹⁵Cd	β⁻, γ	2.5d.	1.11(β⁻) / 0.55(γ)	Cd, n-γ / Cd, n-2n / U, n
¹¹⁷Cd	β⁻	3.75h.		Cd, d-p / Cd, n-γ / U, n
Cd*	I.T., e⁻	50m.		Cd, n-n / U, n(?)
¹¹⁰In	β⁺	65m.	1.6	Cd, p-n
¹¹⁰In	β⁺, γ, e⁻	20m.	1.7(β⁺) / 0.16(γ)	Ag, α-n / Cd, d-2n / Cd, p-n
¹¹²In	K, γ, e⁻	2.7d.	0.17, 0.25(γ)	Ag, α-n

Right portion:

Radio-element	Type of Radiation	Half-Life	Energy of Radiation M.ev.	Method of Production
¹¹²In	K, γ, e⁻	2.7d.	0.17, 0.25(γ)	Ag, α-n / Cd, p-n
¹¹³In*	I.T., γ, e⁻	105m.	0.39(γ)	In, d-p / Cd, d-n / ¹¹³Sn, K decay
¹¹⁴In	I.T., e⁻	48d.	0.19(γ)	Cd, d-n / In, n-γ / Cd, p-n / In, d-p
¹¹⁴In	β⁻	72s.	1.98	Cd, d-n / In, n-2n / ¹¹⁴In, (48d.) I.T. / In, n-2n
¹¹⁵In*	I.T., e⁻, γ	4.1h.	0.34(γ)	In, γ-n / Cd, p-n / In, n-n / In, p-n / In, α-n / In, X-rays / ¹¹⁵Cd, β⁻ decay
¹¹⁶In	β⁻	13s.	2.8	Cd, d-n / In, n-γ / In, d-p
¹¹⁶In	β⁻, γ	54m.	0.85(β⁻), 1.8, 1.4, 1.0, 0.6, 0.4, 0.2(γ)	Cd, p-n / In, n-γ / Cd, p-n / In, d-p
¹¹⁷In	β⁻, γ, e⁻	117m.	1.73(β⁻)	¹¹⁷Cd, β⁻ decay / Cd, d-n
¹¹³Sn	K, e⁻, γ	70–105d.	0.085(γ)	In, p-n / Sn, d-p / Cd, α-n

TABLE XVI—Continued

Radio-element	Type of Radiation	Half-Life	Energy of Radiation M.e.v.	Method of Production	Radio-element	Type of Radiation	Half-Life	Energy of Radiation M.e.v.	Method of Production
<119Sn	β^-	25m.		Cd, α–n	<126Sb	β^-	~2y.		Sn, d–n
<119Sn	β^-	3h.		Cd, α–n	125Sb	β^-	80h.		U, n
<119Sn	β^-	13d.		Cd, α–n	129Sb	β^-	4.2h.		U, n
<125Sn	β^-	40m.		Sn, d–p; Sn, n–γ; Sn, n–$2n$	>131Sb	β^-	<10m.		U, n; Th, n
<126Sn	β^-	26h.		Sn, d–p; Sn, n–γ	>131Sb	β^-	<10m.		U, n
<126Sn	β^-	10d.		Sn, d–p; Sn, n–γ	>131Sb	β^-	5m.		U, n
<128Sn	β^-	~400d.		Sn, d–p	127Te	K, e^-	125d.		Sb, d–$2n$; Sn, α–n; Sb, p–n
125Sn	β^-	9m.		Sn, d–p; Sn, p–n	127Te	I.T., e^-	90d.	0.10(γ)	Te, d–p; I, n–p
Sb	β^-	3.5m.			127Te	β^-	9.3h.		Te, d–p; I, n–p; Te, n–$2n$; 127Te, (90d.), I.T.; 125Sb, β^- decay
$116,118$Sb	β^+	3.6m.		In, α–n	129Te	I.T., e^-	32d.	0.10(γ)	Te, d–p; Te, n–$2n$
129Sb	β^+	17m.	1.53	Sb, n–$2n$; Sb, n–γ; Sn, d–$2n$	129Te	β^-	72m.		Te, d–p; Te, γ–n; Te, n–$2n$; 129Te, (30d.) I.T.; 129Sb, β^- decay
125Sb	β^-	2.8	0.81, 1.64(β^-) 0.96γ	Sn, p–n; Sb, d–p; Sb, n–γ	131Te	I.T., e^-	30h.	0.17(γ)	Te, d–p; U, n
124Sb	β^-	60d.	1.53(β^-) 1.82(γ)	Sn, d–$2n$; Sn, p–n; Sb, d–p; Sb, n–γ	131Te	β^-	25m.		Te, d–p; Te, n–γ; U, n
<126Sb	β^-	3h.		I, n–α; Sn, d–n					
<126Sb	β^-	~45d.		Sn, d–n					

TABLE XVI—Continued

Radio-element	Type of Radiation	Half-Life	Energy of Radiation M.e.v.	Method of Production	Radio-element	Type of Radiation	Half-Life	Energy of Radiation M.e.v.	Method of Production
131Te	β-	25m.		131Te, (30h.) I.T.	127Xe	e-,γ	34d.	0.9(e-)	I, p-n
>131Te	β-	43m.		>131Sb, (<10m.), β- decay	129Xe	β-	<0.5m.		U. n; Th. n
131Te	β-	60m.		>131Sb, (<10m.) β- decay	>131Xe	I.T., e-	4.3d.	0.083(γ)	>131I, (22h.) β- decay
131Te	β-	77h.		>131Sb, (5m). β- decay; Th. n	>131Xe		5d.		Cs, n-p; Ba, n-α
>131Te	β-	~15m.		U. n; Th. n	135Xe		9.4h.		>131I, (6.6h.) β- decay; Ba, n-α
124I	β+	4.0d.		Sb, α-n	Xe	β-	<0.5m.		U. n; Th. n
126I	β-,γ	13d.	1.1(β-); 0.5(γ)	Sb, α-n; I, n-2n; Te, d-n; Te, p-n	>129Xe	β-	17m.		U. n; Th. n
128I	β-,γ	25m.	1.2, 2.1(β-); 0.4(γ)	I, n-α; Te, d-2n; Te, p-n; Te, d-2n; Te, p-n	134Cs	β-	3h.	1	Cs, n-γ; Cs, d-p
130I	β-,γ	12.6h.	0.83(β-); 0.6(γ)	Cs, n-α; Te, d-n	134Cs	β-,γ	1.7y.		Cs, n-γ; Cs, d-p
131I	β-,γ	8.0d.	0.687(β-); 0.4(γ)	131Te, β- decay; >131Te, (77h.) β- decay; >131Te, (43m.) β- decay; >131Te, (~15m.) β- decay	Cs	β-	40s.	0.9(β-)	Xe, (<0.5m.) β- decay
>131I	β-	2.4h.		131Te, (60m.) β- decay	>139Cs	β-	33m.	2.6	>139Xe, (17m.) β- decay; Pa, n
>131I	β-	54m.			133Ba	e-,γ	30h.	0.30(γ)	Ba, n-2n; Ba, d-p; Ba, n-γ
>131I	β-	6.6h.			139Ba	β-	86m.	1(β-); 0.6(γ)	La, n-p; 139Cs, β- decay
>131I	β-	22h.			Ba	β-	3m.		Ba, n-?
137Xe	I.T.(?), e-	75s.	0.175, 0.125(γ)	I, p-n	Ba	β-	~300h.		Cs, (40s.) β- decay
					>140Ba	β-	14m.		U. n; Th. n
					>140Ba	β-	<1m.		U. n

TABLE XVI—Continued

Radio-element	Type of Radiation	Half-Life	Energy of Radiation M.e.v.	Method of Production
¹³⁸La	β⁻	2.2h.	0.8	La, n-2n(?)
¹⁴⁰La	β⁻	31h.		La, d-p
>¹⁴⁰La	β⁻	2.5h.		La, n-γ; >¹⁴⁰Ba, (14m.) β⁻ decay; Th, n
>¹⁴⁰La	β⁻	<30m.		>¹⁴⁰Ba, (<1m.) β⁻ decay
La	β⁻	36h.		Ba, (~300h.) β⁻ decay
¹³⁹Ce	β⁺	2.1m.	0.12(β)	Ce, n-2n(?)
¹⁴¹,¹⁴³Ce	β⁺	15d.		Ce, n-γ
¹⁴⁰,¹⁴²Pr	β⁺	3.5m.		Pr, n-2n or Pr, n-γ
¹⁴³Pr	β⁻	18.7h.		Pr, n-γ
¹⁴⁷Nd	β⁻	84h.		Nd, n-p; Nd, d-p; Nd, n-γ; Nd, n-2n(?)
¹⁴⁹Nd	β⁻	2.0h.		Nd, d-p; Nd, n-γ; Nd, n-2n(?)
¹⁵¹Nd	β⁻	21m.		Nd, n-γ; Nd, d-n
61	β⁻	12.5h.		Sm, n-γ
Sm	β⁻	21m.		Sm, n-2n(?)
Sm	β⁻	46h.		Sm, n-γ; Sm, n-2n(?)
¹⁵⁰Eu	β⁺	27h.	1.88(β⁻)	Eu, n-2n(?)
¹⁵²,¹⁵⁴Eu	β⁻, γ, e⁻ K(?)	9.2h.	0.123, 0.163, 0.725(γ)	Eu, n-γ; Eu, n-2n(?); Eu, d-p
¹⁵²,¹⁵⁴Eu	β⁻, γ	>1y.	0.8(β⁻)	Eu, n-γ
¹⁵²,¹⁵⁴Eu		12m.		Eu, d-p
¹⁵²,¹⁵⁴Eu		105m.		Eu, d-p
¹⁵⁹,¹⁶¹Gd		8h.		Gd, n-γ
¹⁶⁰Tb	β⁻	3.9h.		Tb, n-γ
¹⁶⁵Dy	β⁻	2.5h.	1.9	Dy, n-γ
Dy(?)	β⁺	2.2m.		Dy, n-?
¹⁶⁴Ho	β⁻	47m.		Ho, n-2n(?)
¹⁶⁶Ho	β⁻	35h.		Ho, n-γ
¹⁶⁵Er	β⁺	1.1m.	1.6	Er, n-2n(?)
¹⁶⁹,¹⁷¹Er	β⁺	7m.		Er, n-γ
¹⁶⁹,¹⁷¹Er		12h.		Er, n-γ
¹⁷⁰Tm	β⁻	105d.		Tm, n-γ
¹⁷⁵,¹⁷⁷Yb		3.5h.		Yb, n-γ
Yb(?)		41h.		Yb, n-γ(?)
¹⁷⁵,¹⁷⁷Lu		4h.		Lu, n-γ
¹⁷⁶,¹⁷⁷Lu		6d.		Lu, n-γ
¹⁸¹Hf	β⁻	55d.		Hf, n-γ
¹⁸⁰Ta		14-21m.		Ta, γ-n; (Ta, n-2n)(?)
¹⁸⁰Ta	K, e⁻, γ	8.2h.	<0.5(e⁻)	Ta, n-2n
¹⁸²Ta	β⁻	97d.		Ta, n-γ
¹⁹⁵W	β⁻, γ	77d.	0.4-0.5(β⁻)	Ta, d-p; W, n-γ; W, n-2n
¹⁸⁷W	β⁻, γ	23h.	1.1(β⁻)	W, n-γ; W, n-2n
Re	β⁺	41-55m.		W, p-n
Re		13m.		Re, p-n
Re		>40d.		W, p-n
¹⁸⁶Re	β⁻	90h.	1.05	Re, n-γ

106

TABLE XVI—Continued

Radio-element	Type of Radiation	Half-Life	Energy of Radiation M.e.v.	Method of Production
^{186}Re	β^-	90h.	1.05	Re, n-2n; W, p-n; W, d-2n
^{188}Re	β^-	18h.	2.5	Re, n-γ
^{191}Os	β^-	32h.	1.5	Os, n-2n(?)
^{191,193}Os	β^-	40h.		Os, n-γ
^{193}Os	β^-	17d.	0.35	Os, n-?
^{192,194}Ir	β^-	1.5m.		Ir, n-γ
^{192,194}Ir	β^-	19h.	2.2	Ir, n-γ; Au, d-α, p(?)
^{192,194}Ir	β^-	60d.		Ir, n-γ
^{197}Pt	β^-	18h.		Pt, n-γ; Pt, d-p
^{197}Pt	β^-	3.3d.		Pt, n-γ
^{199}Pt	β^-	31m.		Pt, n-γ; Pt, d-p
^{196}Au	β^-	13h.		Au, n-2n
^{198}Au	β^-, γ	4–5d.	0.36(β^-), 0.41(γ)	Au, n-2n
^{198}Au	β^-, γ	2.7d.	0.8(β^-), 0.28, 0.44, 2.5(γ)	Au, n-γ; Au, d-p
^{199}Au	β^-	3.3d.	<0.4(e^-)	^{199}Pt, β^- decay
^{197}Hg	K, e^-, γ	43m.	<0.25(γ)	Hg, n-2n
^{203,205}Hg		25h.		Hg, n-γ

Radio-element	Type of Radiation	Half-Life	Energy of Radiation M.e.v.	Method of Production
^{206}Tl		4m.	1.6	Au, α-n(?)
^{206}Tl		3.8h.		Au, α-n(?)
^{204}Tl	β^-	4.23m.		Tl, n-γ; Tl, d-p
^{206}Tl	β^-	1–2y.		Tl, n-2n; Tl, n-γ; Tl, d-p
^{205}Pb		80m.	~0.5(γ)	Pb, n-2n
^{204,206}Pb*	I.T.. (?), e^-, γ	52h.		Tl, d-n
^{209}Pb	β^-	3h.	~0.3(γ)	Pb, d-p
Pb*	I.T., e^-	1.6m.		Pb, X-rays
^{210}Bi	β^-	5d.		Bi, d-p; Bi, n-γ
^{210}Po	α	136d.		^{210}Bi, β^- decay; Bi, d-n
^{211}Po	α	$\sim 10^{-8}$s.	7.5(α)	^{211}85, K decay
^{211}85	α, K	7.5h.	6(α)	Bi, α-2n
^{235}UY	β^-	24.5h.		Th, n-2n
^{233}Th	β^-	26m.		Th, n-γ.
^{233}Pa	β^-	25d.		^{233}Th, β^- decay
^{239}U	β^-	23m.		U, n-γ
^{231}U	β^-, γ	~7d.	0.26(β^-)	U, n-2n
^{239}93	β^-	2.3d.	0.47(β^-), 0.22, 0.27(γ)	^{239}U, β^- decay

than α-particles have been employed.   As examples we may cite carbon bombarded with protons to yield ^{13}N with a half-life of 10 min., carbon bombarded with deuterons to yield ^{13}N and the same half-life period.   Longer half-lives obtain with ^{34}Cl from bombardment of phosphorus with α-particles (33 min. half-life), and with ^{42}Sc with a positron activity of 13.5 days half-life.

(60) **Positron Production from γ-Radiation:**   It was quickly found that positrons also resulted from the interaction of hard γ-rays with metals such as lead.[1, 2, 3, 4]   Thus, the γ-rays from ThC′, having energies of 2.6 M.e.v., absorbed by a lead target were shown to produce positron-electron pairs whose tracks are visible in the cloud-chamber, and, originating at one point in the metal are deflected in opposite directions by a magnetic field.   The Curie-Joliots showed similar paired tracks when γ-rays from ThC′ impinged on argon atoms in the cloud chamber.

The neutrons (see Section 51) produced by the α-particle-beryllium technique are also accompanied by penetrating γ-radiation.   Sources consisting of beryllium-polonium with energies of γ-radiation equal to 5 M.e.v. were employed by the Curie-Joliots and others for the production of positron-electron pairs in cloud chambers situated within a strong magnetic field.   In such experiments, an excess of electrons over positrons is always found; the electronic absorption coefficient is in excess of that which would be computed on the basis of the photoelectric and Compton effects produced by the γ-radiation.   The excess reaches as much as 20 per cent of the total with γ-radiation from ThC′ and with elements of high atomic number.   With γ-radiation of higher energies, the "excess" absorption reaches 60 per cent for radiation of 5.4 M.e.v.[5] and more than 90 per cent with radiation of 12 M.e.v.[6]   It is assumed that the excess absorption is to be ascribed to production of positron-electron pairs by annihilation of γ-radiation and the extensive cloud-chamber experiments of Chadwick, Blackett and Occhialini confirm this conclusion.

(61) **Mass and Charge of the Positron:**   The γ-rays from ThC′, with an energy of 2.6 M.e.v., produce both in lead and aluminum foils positive particles whose maximum energies are 1.6 M.e.v., with values for the energies of many not more than half this value.   In the production of positron-electron pairs by the same radiation it was found that their joint energies were 1.6 M.e.v. although many electrons with energies up to 2.6 M.e.v. are observed.   These latter obviously arise from the extra-nuclear electrons of the atoms which are the most loosely bound.   More accurate measurements gave a maximum positron energy from this source as 1.55 ± 0.03 M.e.v.   The same authors [7] found that electron and positron have the same value for e/m within an error

[1] J. Chadwick, P. M. S. Blackett and G. Occhialini, *Nature*, **131**, 473 (1933).

[2] C. Anderson and S. H. Neddermeyer, *Phys. Rev.*, **43**, 1034 (1933).

[3] I. Curie and F. Joliot, *Compt. rend.*, **196**, 1581 (1933).

[4] L. Meitner and K. Philipp, *Naturwiss.*, **21**, 468 (1933).

[5] E. McMillan, *Phys. Rev.*, **46**, 325A (1934).

[6] H. R. Crane, L. A. Delsasso, W. A. Fowler and C. C. Lauritsen, *ibid.*, **46**, 531 (1934).

[7] J. Chadwick, P. M. S. Blackett and G. Occhialini, *Proc. Roy. Soc.*, [A], **144**, 241 (1934).

of two per cent. The rest-mass of an electron, 0.00055 on the atomic weight scale, corresponds to 0.5 M.e.v. of energy. Thus, the difference in energy between the γ-radiation and the average positron-electron pair is wholly accounted for in terms of the masses of positron and electron formed.

The identity of e/m for positron and electron within an error of less than one per cent has recently been demonstrated by Zahn and Spees [1] using a method developed by them for their work on the specific charge of β-rays from RaE. Data on the positron and electron were obtained with the aid of the radioactive isotope of copper, ^{64}Cu, which emits both positrons and electrons, with a half-life of 12.8 hours. By reversing electric and magnetic fields measurement could be changed from electron to positron without disturbing the geometry of the apparatus. Peaks corresponding to maximum number of particles transmitted as a function of the electric field were found to have the same position for both types of particles, within the accuracy of one per cent.

(62) **The Fate of the Positron:** In contrast to the electron, the positron is very short-lived. Within a period of the order of 5×10^{-10} sec. it will have lost the greater part of its kinetic energy and is then annihilated by interaction with an electron with the simultaneous production, to conserve momentum, of two γ-ray photons whose joint energy, from the considerations advanced in the previous section, must be approximately 1 M.e.v. Experiments of Chao [2] and of Gray and Tarrant [3] demonstrated the existence of a secondary isotropic radiation with an energy of about 0.5 M.e.v.

(63) **Nuclear Fission:** [4] A new type of nuclear process involving neutron interaction was discovered by Hahn and Strassmann [5] early in 1939, the novelty of which is abundantly evidenced by the appearance of some one hundred papers dealing with the subject in the intervening months. The work which culminated in this discovery began in 1934 when Fermi [6] examined the bombardment of uranium by neutrons, a process which might be expected to produce atoms with an atomic number of 93. With his collaborators, Fermi had shown [7] that nuclei resulting from the capture of neutrons were unstable and reverted to stability by the ejection of beta-particles, a process which produces nuclei whose atomic number is one greater than the bombarded nucleus. Observations of neutron interaction with thorium and uranium showed two and four or possibly five beta-ray activities respectively. These results pointed to the occurrence of unusual processes since only three isotopes of uranium were known. Element No. 93 would be a seventh group element in the series, $_{25}$Mn, $_{43}$Ma, $_{75}$Re and so precipitation of irradiated uranium with added manganese

[1] C. T. Zahn and A. H. Spees, *Phys. Rev.*, **53**, 365 (1938).

[2] C. Y. Chao, *Proc. Nat. Acad. Sci.*, **16**, 431 (1930); *Phys. Rev.*, **36**, 1519 (1930).

[3] L. H. Gray and G. T. P. Tarrant, *Proc. Roy. Soc.*, [A], **136**, 662 (1932); **143**, 681 (1934).

[4] This section is based upon a comprehensive review of the subject by L. A. Turner, *Rev. Mod. Phys.*, **12**, 1 (1940).

[5] O. Hahn and F. Strassmann, *Naturwiss.*, **27**, 11, 89 (1939).

[6] E. Fermi, *Nature*, **133**, 898 (1934).

[7] E. Fermi, E. Amaldi, O. D'Agostino, F. Rassetti and E. Segrè, *Proc. Roy. Soc.*, [A], **146** 483 (1934).

salts as MnO_2 was studied.   Two of the activities with approximately 13 and 90 minute half-lives were brought down partially in this manner but no activities of $_{92}U$, $_{90}UX_1$, or $_{91}UX_2(Pa)$ were detected in the precipitate.   Additional experiments showed that the activities were not ascribable to isotopes of any of the elements from radon to uranium inclusive (86–92).   The process of interaction of uranium with neutrons was therefore not capture with beta-ray emission, nor an $(n-p)$ nor an $(n-\alpha)$ process.   The hypothesis was therefore adopted that the activities observed were due to trans-uranic elements of atomic number 93 and higher.

It was pointed out by Noddack [1] that precipitation with manganese dioxide was not compelling evidence of seventh group elements since other elements are precipitated, for example, polonium $_{84}Po$.   She also pointed out that a rigorous proof that the new substances were trans-uranic elements would require exclusion of all known elements including those which might be formed by the splitting of bombarded nuclei to form elements of lower atomic number.   Von Grosse and Agruss [2] showed that $_{91}Pa$ was also precipitated with MnO_2 and with rhenium sulfide and suggested that the new material might be in part a new isotope of element 91.   This was tested by Agostino and Segrè [3] and disproved.   Hahn and Meitner [4] intervened to test also the assignment of the 13 min. and 90 min. activities to an isotope of $_{91}Pa$, utilizing a new technique. Using potassium perrhenate and platinic chloride as the added agents for the precipitation technique they showed that, after precipitation with sodium hydroxide which should have removed quantitatively elements Nos. 90, 91 and 92 but not elements higher than 92, the activity remained in the filtrate and, on weak acidification with hydrochloric acid, came down with platinum as the sulfides on treatment with hydrogen sulfide.   With stronger acidity, the rhenium was also precipitated.   The 13-min. and 90-min. activities were therefore not attributable to isotopes of elements 90, 91 and 92 but to elements somewhat more like platinum than rhenium.

With thorium, the products reported by Fermi were shown to have half-lives of 1 and 24 min., the latter attributable to an isotope of thorium, possibly a member of the missing $4n + 1$ family of radioactive bodies.   The mass numbers of the known Th, U and Ac series are representable by $4n$, $4n + 2$ and $4n + 3$ respectively.   Hahn and Meitner [5] stressed this possibility and both they and Curie, von Halban and Preiswerk [6] found that the 24-min. product was enhanced by the use of slow neutrons (paraffin technique) and identified it as an active thorium.   A 2.5 min. product found by the latter authors was identified as a $_{91}Pa$ isotope and the 1 min. product precipitable with barium was

[1] I. Noddack, Z. angew. Chem., **37**, 653 (1934).

[2] A. von Grosse and M. S. Agruss, J. Am. Chem. Soc., **57**, 488 (1935).

[3] O. D'Agostino and E. Segrè, Gazz. Chim. Ital., **65**, 1088 (1935).

[4] O. Hahn and L. Meitner, Naturwiss., **23**, 37, 230 (1935).

[5] O. Hahn and L. Meitner, Naturwiss., **23**, 320 (1935).

[6] I. Curie, H. von Halban and P. Preiswerk, J. phys. Radium, **6**, 361 (1935); Compt. rend., **200**, 1841, 2079 (1935).

identified as an isotope of $_{88}$Ra. This radium would necessarily be the product of an $(n-\alpha)$ process which does not occur for other heavy nuclei owing to the high potential energy barrier. Products with 12 min. and 3.5 hr. half-lives had the chemical properties of lanthanum and were attributed to actinium.

As a result of further work, Meitner, Hahn and Strassmann [1] came to the conclusion that slow and fast neutrons were capable of producing three different active isotopes of uranium which decayed by successive β-ray disintegrations in three separate ways:

1. $_{92}$U $+ n \rightarrow _{92}$U(10 sec.) $\rightarrow _{93}$Eka Re(2·2 min.) $\rightarrow _{94}$Eka Os(59 min.)—
   $\rightarrow _{95}$Eka Ir(66 hr.) $\rightarrow _{96}$Eka Pt(2.5 hr.) $\rightarrow _{97}$Eka Au(?).

2. $_{92}$U $+ n \rightarrow _{92}$U(40 sec.) $\rightarrow _{93}$Eka Re(16 min.) $\rightarrow _{94}$Eka Os(5.7 hr.)—
   $\rightarrow _{95}$Eka Ir(?) $\rightarrow$

3. $_{92}$U $+ n \rightarrow _{92}$U(23 min.) $\rightarrow _{93}$Eka Re(?) $\rightarrow$

The uranium isotope with 23 minute life was positively identified by the sodium uranyl acetate precipitation, and, occurring with slow neutrons only, it is a typical case of neutron capture. The large measure of neutron absorption found in this process was compatible only with absorption by the abundant isotope ^{238}U. The 23 min. isotope became therefore ^{239}U. The 10 sec. and 2.5 hr. isotopes were less positively identified as uranium isotopes. The products of sequences (1) and (2) were produced both by fast neutrons (Ra-Be) and thermal neutrons. The probabilities of the two processes appeared equal and the relative amounts of the products were independent of the neutrons employed, whether thermal or fast, and the absorption of the neutrons indicated the abundant isotope ^{238}U as the source. Detailed comparisons of the properties of the products with their supposedly chemical analogues were given in a subsequent paper [2] which comparisons, while moderately successfully supporting the disintegration schemes just cited, very definitely raised problems of isomerism of uranium nuclei of mass 239, and an isomerism of such a nature that so diverse and so prolonged series of emissions were initiated.

Meanwhile Curie and Savitch [3] produced products by a modified technique with half-lives of 3.5 hr., 16 min., 2 min., and $\sim$ 40 sec. Chemical tests showed that the 3.5 hr. product was precipitable with lanthanum, and more closely related to this element than to actinium of which it might possibly have been the $(n-\alpha)$ isotope $_{89}$Ac. They believed that it was so like lanthanum that it could only be separated by fractionation of which they obtained some evidence. Actually it is now known that what they then obtained was lanthanum and their fractionation may have been the separation of an yttrium isotope of the same half-life. They showed that their 3.5 hr. body could not have been derived from any active substance with a half-life of more than 0.5 hr. The

[1] L. Meitner, O. Hahn and F. Strassmann, *Z. Physik*, **106**, 249 (1937).
[2] O. Hahn, L. Meitner and F. Strassmann, *Ber.*, **70**, 1374 (1937).
[3] I. Curie and P. Savitch, *J. phys. Radium*, **8**, 385 (1937); **9**, 355 (1938).

assumption that it was a trans-uranic substance and yet chemically similar to lanthanum in a region of the periodic table beyond uranium was one more puzzle that the trans-uranic theory posed.

The experiments just recorded led Hahn and Strassmann to repetition of their studies, with the result that these authors, using barium and lanthanum as carriers, found that it was possible to precipitate active bodies with both elements. With the Ba precipitate substances of half-lives of 25 min., 110 min. and several days were identified and, from these, daughter substances with half-lives of 40 min., 4 hr., and 60 hr., precipitable with lanthanum resulted. They were,[1] it was suggested, isomeric $_{88}^{231}$Ra-nuclei and $_{89}^{231}$Ac-nuclei respectively. Again arose the problem of threefold-isomerism of nuclei, arising from ^{239}U by ejection of two alpha-particles. Search by various workers for these alpha-particles was unsuccessful.

To confirm the chemical evidence obtained in their preceding studies Hahn and Strassmann initiated elaborate tests to prove rigorously the nature of their active products. In so doing they found evidence for a fourth 'Ra' and a corresponding fourth 'Ac.'[2] Their next test was fundamental and established the existence of nuclear fission. Using the well-known techniques employed in separating radium from barium in radio-chemistry they succeeded, contrary to their expectations, in showing that the RaIV, with a half-life of 250–300 hr., was an isotope of barium rather than of radium. They forced themselves as chemists to the conclusion "that the new bodies are not radium but barium; that elements other than barium and radium are not involved." The next test was decisive, for, if the parents were a group of active bariums, the daughters should be active lanthanums and not actinium isotopes. "Actinium II" with a half-life of 2.5 hr., remained with the lanthanum fraction when admixed with a solution containing both lanthanum and MsTh$_2$, the latter an isotope of actinium which concentrated in the oxalate precipitation.

The reserve with which their conclusions were reached was rendered unnecessary by their subsequent publication.[3] Both RaIII and RaIV were shown to be isotopes of barium; the "radiums" from bombarded thorium were also shown to be barium isotopes, some of which were identical with barium isotopes known from other work. The half-life of 86 minutes of one such product agrees well with the ^{139}Ba of half-life 85 min. produced by beta-particle emission from ^{139}Cs. RaIV with a half life of < 40 hr. has been identified with the known ^{140}La, of half life 31–46 hr., produced by a $(d—p)$ reaction from the stable lanthanum isotope ^{139}La.

From a uranium isotope ^{239}U the fission of a barium nucleus of mass 139 must leave a residue of mass $\sim$ 100. Hahn and Strassmann found an active strontium and an active yttrium. A gas swept out of the solution of the bombarded uranium gave active deposits which precipitated with both strontium and cesium, indicating both active krypton and xenon in the gas.
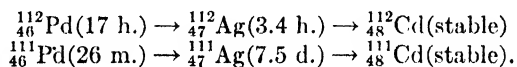
[1] O. Hahn and F. Strassmann, *Naturwiss.*, **26**, 755 (1938).

[2] O. Hahn and F. Strassmann, *ibid.*, **27**, 11 (1939).

[3] O. Hahn and F. Strassmann, *ibid.*, **27**, 89 (1939).

In the two years which have elapsed since these discoveries there has occurred an extraordinary activity in confirmation and extension of the phenomenon of fission. Turner summarized the chemically identified fission products from uranium and thorium as follows: $_{51}$Sb(The atomic number precedes the symbol; the masses of the nuclei found are placed in parentheses) $_{34}$Se(?); $_{35}$Br(82); $_{36}$Kr(83 and 88); $_{37}$Rb(88); $_{38}$Sr(89, a); $_{39}$Y(> 90); $_{42}$Mo(99 or 101); $_{43}$Ma(99 or 101); $_{47}$Ag(?); $_{51}$Sb(127, 129, 132, a, b); $_{52}$Te(127, 129, 131, 132, a, b); $_{53}$I(131, 132, a, b); $_{54}$Xe(139, 140?, ?); $_{55}$Cs(139, 140?, ?); $_{56}$Ba(139, 140? a, b); $_{57}$La(140?, a, b, ?). Grosse and Booth [1] found the two missing elements in the light-weight group, $_{40}$Zr and $_{41}$Cb, the former with a 17.0 h. period and the latter with a 75 m. period as a daughter product. As indicated below, the elements with atomic numbers between 43 and 51 do not appear with neutrons of energy up to $\sim$ 10 M.e.v. but are being found with energies of $\sim$ 17 M.e.v. Von Grosse, Booth and Dunning [2] have found fission of protoactinium with fast neutrons, but not with thermal neutrons. Roberts, Meyer and Hafstad [3] found no fission equal to 1/1000 of that with thorium by fast neutron bombardment (up to 13 M.e.v.) of Bi, Pb, Tl, Hg, Au, Pt, W, Sn, Ag.

(64) **Neutron Energy and Nuclear Fission:** It is now known that the fission process and its nature is dependent both on the energy of the neutron and on the isotope of uranium which is bombarded. As already mentioned, with neutron energies up to $\sim$ 10 M.e.v. no fission products of uranium or thorium with atomic numbers between 43 and 51 have been reported. Nishina, and his collaborators,[4] as well as Segrè and Seaborg [5] now report fission products of uranium and thorium in this range with neutron energies of $\sim$ 17 M.e.v. Radioactive isotopes of palladium, silver, cadmium and indium have been found. Segrè and Seaborg report two chains from both fission elements having the characteristics:

$$_{46}^{112}\text{Pd}(17 \text{ h.}) \rightarrow {}_{47}^{112}\text{Ag}(3.4 \text{ h.}) \rightarrow {}_{48}^{112}\text{Cd(stable)}$$
$$_{46}^{111}\text{Pd}(26 \text{ m.}) \rightarrow {}_{47}^{111}\text{Ag}(7.5 \text{ d.}) \rightarrow {}_{48}^{111}\text{Cd(stable)}.$$

The isotopic assignments are based upon the identifications of the two silver isotopes ^{111}Ag and ^{112}Ag. They have also examined a 4 h. activity which was presumably that of radioactive ruthenium, $_{44}$Ru. Nishina and Yasaki, Kimura and Ikawa confirm both the existence of the ruthenium and rhodium isotopes,[6] separated as sulfide and metal respectively from uranium oxide irradiated with fast neutrons. The rhodium fraction shows a decay curve of a single period of 34 h., while the ruthenium portion gave two periods of about 4 and 60 h. The rhodium decay is an electron emission, the period suggesting

[1] A. von Grosse and E. T. Booth, *Phys. Rev.*, **57**, 664 (1940).
[2] A. von Grosse, E. T. Booth and J. R. Dunning, *ibid.*, **56**, 382 (1939).
[3] R. B. Roberts, R. C. Meyer and L. R. Hafstad, *ibid.*, **55**, 416 (1939).
[4] Y. Nishina, T. Yasaki, H. Ezoe, K. Kimura and M. Ikawa, *ibid.*, **58**, 660 (1940).
[5] E. Segrè and G. T. Seaborg, *ibid.*, **59**, 212 (1941).
[6] Y. Nishina and T. Yasaki, K. Kimura and M. Ikawa, *ibid.*, **59**, 323, 677 (1941).

an isotope of mass greater than 105 and yielding, probably, a stable palladium isotope of mass either 106, 108 or 110. The ruthenium period of 4 h. has been shown to be the mother substance of the 34 h. rhodium and the 60 h. decay first reported is found to be, in reality, a superposition of the growth and decay curve of the 34 h. rhodium produced from the 4 h. ruthenium.

Both fast neutrons (with energies greater than 0.5 M.e.v.) and very slow thermal neutrons (with energies of $\sim$ 0.025 M.e.v.) are effective in producing uranium fission. In addition, ^{239}U is produced by a strong resonance absorption with a large cross-section at 25 e.v. The ^{239}U emits electrons giving element 93. The cross-section for fast neutrons rises rapidly with neutron-energies from 0.5 to 2 M.e.v. and then does not markedly increase at high energies. The fission cross-section for thermal neutrons is as much as 40 times that of the cross-section for fast neutrons. By experiments on the bombardment of the separated isotopes of uranium carried out by Nier, Booth, Dunning and Grosse,[1] Kingdon and Pollock,[2] it is now certain that it is the uranium isotope ^{235}U which undergoes the major portion of the fission with thermal neutrons. This isotope is present to the extent of 1 part in 140 of the total, the isotope of mass 238 being 139 times more abundant and the isotope of mass 234 being only 0.006 per cent of the total. The several isotopes were separated by means of the mass spectrograph and the number of fissions per unit time observed after the separated samples had been irradiated with thermal neutrons. While it cannot yet be excluded that ^{234}U undergoes some slow neutron fission, its total contribution, if any, must be small. The results show conclusively that the abundant isotope ^{238}U undergoes fast neutron fission only and is responsible for practically all the fast neutron fission observed with unseparated uranium.

(65) **Energy and Range of the Fission Fragments**: The total energy of the fission fragments has been measured by Henderson,[3] who determined the heat produced in a sample of uranium subjected to an intense beam of neutrons. The energy thus determined amounted to 175 M.e.v. $\pm$ 10 per cent. This represents an upper limit, since it includes that heat which is produced in the subsequent β-disintegrations of the fission fragments. Early measurements of the energy liberated compared the ionization produced by the single fission fragments with that produced by α-particles of known energy. Two maxima were observed in the number-ionization curves and the energy-sum corresponded to from 125 to 160 M.e.v.[4] More precise measurements by Kanner and Barschall [5] show that the number-energy curve shows two peaks corresponding to 65 and 98 M.e.v. The ionization produced simultaneously by the two fragments was measured by using a very thin foil coated with uranium. The number-energy curve has then one peak with 159 M.e.v. and a half-width

[1] A. O. Nier, E. T. Booth, J. R. Dunning and A. von Grosse, *ibid.*, **57**, 546, 748 (1940).

[2] K. H. Kingdon, H. C. Pollock, E. T. Booth and J. R. Dunning, *ibid.*, **57**, 749 (1940).

[3] M. C. Henderson, *ibid.*, **56**, 703 (1939).

[4] W. Jentsche and F. Prantl, *Naturwiss.*, **27**, 134 (1939); E. T. Booth, J. R. Dunning and F. G. Slack, *Phys. Rev.*, **55**, 981 (1939).

[5] M. H. Kanner and H. H. Barschall, *ibid.*, **57**, 372 (1940).

of 30 M.e.v.   These results are in good agreement with the data of Jentsche and Prantl.   The energy ratio of the two peaks should be inversely proportional to the mass ratio of the fission fragments.   For the ^{239}U nucleus this would give, as the masses of the most probable fragments, 96 and 143, which are quite compatible with observed fragments.   The result is also in good agreement with the theoretical conclusions of Bohr and Wheeler.[1]   The data of Booth, Dunning and Slack[2] show that the ranges in air of the two energy groups of fission fragments are 1.5 and 2.2 cm. respectively.

(66) **The Emission of Neutrons in Fission:** The proton-neutron ratio in the uranium nucleus is of such a nature that two fission fragments, with masses distributed around the mean masses of 96 and 143, may be thought of in two ways.   They may be regarded as too feebly charged for their mass, that is to say they will be electron emitters until stable nuclei are produced.   Or, alternatively, they may be thought of as too massive for their charge, and should thus be able to emit neutrons, the energy consumed being about 4 M.e.v. per neutron emitted.   H. von Halban, Joliot and Kowarski[3] determined whether neutrons were produced in the fission process by placing neutron detectors at various distances from a fission source surrounded first by a uranyl nitrate solution and, for comparison, by a solution of ammonium nitrate of the same molar concentration.   Although uranium absorbs neutrons, the average neutron density in the tank was larger when uranium was present than when this was replaced by ammonium salt.   They concluded that 3 to 4 neutrons might be produced per fission.   Zinn and Szilard[4] found a lower figure of 2.3.   These neutrons are emitted within 10^{-3} sec. after fission.[5]   Data by von Halban, Joliot, Kowarski and Perrin[6] give a value of 3.1 secondary neutrons per fission.

(67) **Nuclear Fission as a Chain Process:** The emission of more than one neutron, on the average, as the result of a fission process evidently suggests the possibility of the whole fission reaction as a self-perpetuating or chain process capable of yielding, from an initial neutron-uranium nucleus interaction, a multiplying chain of similar processes.   In view of the extremely high energy yields of each unit fission, the possibility of energy production by these nuclear changes becomes at once a matter of importance.

Early suggestions of the danger of a catastrophic explosion so produced do not now appear to be probable.   On the other hand, careful enquiry is being made into the possibility of gearing such nuclear processes to power production in one or another form.   Absorption of neutrons by other elements than uranium is one method whereby the efficiency of a chain process is decreased.   Further, the fast neutrons produced in the fisssion process must be slowed down to thermal energies before they become efficient as fission agents.   Because of

[1] N. Bohr and J. A. Wheeler, *ibid.*, **56**, 426 (1939).

[2] E. T. Booth, J. R. Dunning and F. G. Slack, *ibid.*, **55**, 981 (1939).

[3] H. von Halban, F. Joliot and L. Kowarski, *Nature*, **143**, 471, 680, 939 (1939).

[4] W. H. Zinn and L. Szilard, *Phys. Rev.*, **55**, 799 (1939).

[5] D. F. Gibbs and G. P. Thomson, *Nature*, **144**, 202 (1939).

[6] H. von Halban, F. Joliot, L. Kowarski and F. Perrin, *J. phys. Radium*, **10**, 428 (1939).

the high uranium mass this slowing-down is very gradual in pure uranium. Neutron-capture to yield ^{239}U constitutes an additional factor decreasing efficiency. Finally, the data cited in Section 64 indicating that it is only the rarer isotope ^{235}U which undergoes fission with thermal neutrons, account also for the decreased probability of a catastrophic change.

It has been pointed out by Adler and von Halban [1] that the development of chains involving slow neutrons can be controlled by the admixture of cadmium with the uranium and hydrogen-containing medium. As energy is released there will be a rise in temperature which will increase the average energy of the thermal neutrons. The number of fissions remains constant, however, since the target-area varies inversely as the neutron-energy. For cadmium, the cross-section is constant and, hence, the number of neutrons removed by cadmium will rise with increasing temperature. A steady state of temperature will thus develop due to the competing processes.

The efficiency of the fission-process as a source of atomic energy would obviously be increased by the concentration of the rarer isotope ^{235}U which is the source of fission with thermal neutrons. Various schemes of isotope separation are being investigated in this case. The separation is obviously a difficult one by reason of the high masses of the isotopic species involved.

(68) **Photo-Fission:** No fission was observed in early experiments [2] with the γ-rays produced by proton bombardment of lithium or fluorine. Later work by Haxby, Shoupp, Stephens and Wells [3] was successful. A beam of 0.5 μa. of protons having 2 to 3 M.e.v. energy was used to bombard calcium and aluminum fluoride targets. With the γ-rays so produced fission recoils from both uranium and thorium targets were observed with cross-sections of 3.5 ± 1.0 and $1.7 \pm 0.5 \times 10^{-27}$ cm.^{2} respectively for the photo-fission process. No fissions were observed with calcium or with aluminum targets. Below 2 M.e.v. the fission rate was too low for observation. With 2.9 M.e.v. protons the observed fission rate in uranium was one fission per 3×10^{13} protons hitting calcium fluoride, the protons being estimated to yield 10^8 γ-quanta. The effect in thorium is roughly equal in intensity.

(69) **Fission by Deuterons and α-Particles:** Fission with 9 M.e.v. deuterons was established by Gant.[4] The yield was small and fell off rapidly with decreasing energy. Jacobsen and Lassen [5] found a rapid rise in fission yield from 8 to 9.5 M.e.v. deuterons. For 9 M.e.v. deuterons the cross-section in uranium is 5×10^{-27} cm.^{2} and the ratio of uranium to thorium cross-section is 0.7.

Fermi and Segrè [6] have shown that 32 M.e.v. α-particles yielded fission with uranium, iodine isotopes I(54 m.), I(3.4 h.), ^{132}I(22 h.) and ^{131}I(8 d.) with

[1] F. Adler and H. von Halban, *Nature*, **143**, 793 (1939).

[2] R. B. Roberts, R. C. Meyer and L. R. Hafstad, *Phys. Rev.*, **55**, 416 (1939); F. A. Heyn, A. H. W. Aten, Jr., and C. J. Bakker, *Nature*, **143**, 516 (1939).

[3] R. O. Haxby, W. E. Shoupp, W. E. Stephens and W. H. Wells, *Phys. Rev.*, **58**, 92 (1940); **59**, 57 (1941).
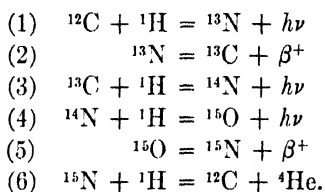
[4] D. H. T. Gant, *Nature*, **144**, 707 (1939).

[5] J. C. Jacobsen and N. O. Lassen, *Phys. Rev.*, **58**, 867 (1940).

[6] E. Fermi and E. Segrè, *ibid.*, **59**, 680 (1941).

tellurium members of the same chains being identified. The possibility of the effect being due to neutron and deuteron contamination was eliminated.

(70) **Thermo-nuclear Processes:** To produce by thermal means the reactions attained by high speed projectiles such as α-particles, protons, deuterons and neutrons, temperatures of one or more million degrees would be necessary for any reasonable rate of change. Actually such temperatures, quite impracticable in the laboratory, occur in the interior of the sun and many stars. The central solar temperature of 20×10^6 degrees makes the occurrence of such nuclear reactions rapid processes in the sun's interior. Indeed, it is now believed that such nuclear reactions are responsible for the enormous energy resources of the sun, which previously had never been satisfactorily explained. Independently, Bethe and Weizsacker found a sequence of nuclear changes which is in satisfactory accord with the best data on the energy output of the sun. The sequence of reactions forms a closed circular chain in which the participants are nuclei of carbon, nitrogen and the thermal protons with which they collide. The sequence may be summarized thus:

$$(1) \quad {}^{12}C + {}^{1}H = {}^{13}N + h\nu$$
$$(2) \quad\quad\quad {}^{13}N = {}^{13}C + \beta^+$$
$$(3) \quad {}^{13}C + {}^{1}H = {}^{14}N + h\nu$$
$$(4) \quad {}^{14}N + {}^{1}H = {}^{15}O + h\nu$$
$$(5) \quad\quad\quad {}^{15}O = {}^{15}N + \beta^+$$
$$(6) \quad {}^{15}N + {}^{1}H = {}^{12}C + {}^{4}He.$$

It will be noted that the ^{12}C consumed in the first reaction is regenerated in the final reaction to permit the repetition of the cycle. The carbon and nitrogen nuclei, ^{12}C and ^{14}N are catalysts for the net overall change which may be represented as the summation of the sequence in the equation

$$4{}^{1}H = {}^{4}He + 2\beta^+ + 3h\nu.$$

Hydrogen, which is present in the sun's atmosphere in abundance (sufficient for 10^9 years yet!), is converted into helium, two positrons and the energy of three γ-rays given in reactions 1, 3 and 4 of the sequence, and of magnitude determined by the mass-energy relation applied to these processes.

CHAPTER II

QUANTUM THEORY OF ATOMIC SPECTRA AND ATOMIC STRUCTURE

BY SAUL DUSHMAN,

Assistant Director, Research Laboratory, General Electric Co., Schenectady, N. Y.

INTRODUCTION

In 1901 there appeared a paper by M. Planck [1] in which he pointed out that the observations on the distribution of energy in black body radiation could not be reconciled with the wave theory of light as formulated by Huyghens and subsequently developed by Clerk Maxwell into the electromagnetic theory of radiation. He therefore suggested the hypothesis that energy is emitted or absorbed discontinuously in multiples of a certain unit or *quantum* of magnitude $h\nu$, where ν is the frequency of the radiation and h is a constant, which has become known as Planck's or the quantum constant. The new theory thus represented, in a limited sense, a return to Newton's corpuscular theory, inasmuch as it assigned to radiation an atomistic structure quite in contradiction with the prevalent or classical point of view.

While Planck's views were applied by A. Einstein to develop a theory of atomic specific heats and also in formulating a relation for the photoelectric effect, it was not until N. Bohr incorporated the quantum hypothesis into a theory of electronic energy levels in atoms, with very striking success, that physicists in general began to realize the generality of these so-called quantum effects. All these phenomena, which are described in the first part of this chapter, have this characteristic in common: the loss in translational energy of an electron, or the loss in vibrational energy of a molecule, is transformed into radiation of frequency ν, where

$$h\nu = \Delta E$$

and ΔE is the loss in kinetic energy. The converse effects are also observed, in which radiant energy of magnitude $h\nu$ is converted into kinetic energy of a corpuscle. It is because of the existence of these effects that these energy-units or quanta have also been designated "light darts" or "photons." In no other phenomenon is the corpuscular nature of radiation exhibited more strikingly than in the Compton effect which is most adequately interpreted as the result of a collision between a photon and an electron. Yet, when we wish to

---

[1] *Ann. Physik*, **4**, 553 (1901).

determine the magnitudes of the energy quanta recourse must be had to a measurement of wave length, i.e., a method which involves the application of the undulatory theory of light.

Until about 1925 this dualistic conception of the nature of radiant energy presented to the physicist a well-nigh insoluble riddle.   At the same time there were encountered more and more difficulties in the efforts to reconcile observations on atomic spectra with the model of atomic structure which Bohr, Sommerfeld and others had built up on the basis of a hybrid theory involving both classical mechanics and quantum conditions.   A much more satisfactory solution was derived, as a result of, firstly, the introduction of the idea of electron spin, and secondly, the discovery of the phenomena of electron diffraction.   The latter necessitated the view that associated with corpuscular motion there exists a wave length, the so-called de Broglie wave length, λ_B, which is intimately connected with the momentum of the particle through the relation

$$\lambda_B = h/mv,$$

where m = mass, and v = velocity of the particle.   Thus, along with the dualistic behavior of radiation, previously regarded as exclusively an undulatory phenomenon, it was found that there also exists a similar dualism in the nature of infinitesimal material particles, inasmuch as their behavior could not be interpreted satisfactorily in terms of classical mechanics.

In attempting to reconcile these apparent contradictions, W. Heisenberg was led to formulate his famous Principle of Indeterminism, which provides the philosophical foundation for the mathematical developments by himself, E. Schroedinger, P. A. M. Dirac and others.   This new technique, known as quantum mechanics, while more difficult to present in terms of naive physical concepts, such as the Bohr electronic orbits, has not only proven much more successful than the latter, in correlating quantitatively the observations on atomic spectra and on electronic behavior, but has also led to the introduction of new concepts, such as those of penetration through potential barriers, and exchange energy.   These deductions from the mathematical derivations of the new mechanics have made possible a more adequate understanding of the observations on transformation in radioactive nuclei on the one hand, and of ferromagnetism and valence bonds on the other.

It is the main object of this chapter to present the experimental observations upon which our present views of the structure of the atom are based. Inasmuch, however, as any satisfactory theory provides an interpretation and correlation of observations of apparently diverse nature, it will also be necessary to present as the occasion demands, some of the simpler mathematical aspects of the new theory and, to a greater extent, the significant physical implications involved.

The first eight sections of the chapter deal with the fundamental observations which lead on the one hand to a corpuscular theory of radiation, and on the other, to a wave theory of corpuscular motion.   These observations may

be designated as *quantum effects* and constitute the basis for the interpretation of a very extensive range of spectroscopic observations which are discussed in the subsequent sections in terms of electronic configuration of atomic systems.

In presenting this material it has been necessary to adopt *self-consistent* values of certain basic physical constants, such as e, the charge on the electron, m, the mass of the electron, h, Planck's constant, and c, the velocity of light, from which a large number of other constants are derived, that are of importance in the discussion of spectroscopic data and atomic behavior.

In 1929, R. T. Birge published a comprehensive and critical survey on this topic [1] and a table of values of physical constants which were accepted for many years as based on the most accurate observations available. During the past few years, as a result of new observations, some question has arisen regarding the accuracy of some of the fundamental constants. For instance, the value accepted in 1929 for e was $(4.770 \pm 0.005) \times 10^{-10}$ absolute electrostatic units. It is now recognized that this value is too low, and more recently Birge has recommended [*] the value 4.8022×10^{-10}, while F. G. Dunnington [2] favors the value $(4.8025 \pm 0.0004) \times 10^{-10}$ e.s.u. and H. T. Wensel,[3] who has also given this topic critical consideration, concludes that the best value is $e = (4.800 \pm 0.004) \times 10^{-10}$ e.s.u. Since one method for the determination of h depends on that of e, it is necessary to assign to the quantum constant a value which is approximately $\frac{3}{4}$ per cent greater than the value $h = (6.547 \pm 0.008) \times 10^{-27}$ erg sec., published in 1929. While Birge's suggested value, based on considerations discussed in a subsequent section, is 6.6236×10^{-27}, both Dunnington and Wensel favor the value 6.610×10^{-27}. It is all a question of deciding between the relative accuracy of different sets of observations and different methods for the derivation of the various constants.

In view of this situation it is impossible, at the time of writing, to assign to some of the fundamental physical constants values upon which there is universal agreement. In fact, it is a question, in some cases, as to which constant is to be regarded as fundamental, and which as derived. It would seem, however, highly desirable that the values of the different constants should form a self-consistent set. For instance, the value of h/e as used in formulae for the photoelectric effect should be the same as that calculated from the Rydberg constant.

In the ensuing chapter the writer has used the values of fundamental physical constants recommended by Birge. The basic constants are given in Table A of the Appendix to this volume; the values of the other constants, derived from those in Table A, are given in Table B. A more detailed discussion of the different observations and relations upon which these derived values are based, will be found in the subsequent sections.

[1] *Phys. Rev.* (Supplement), **1**, 1 (1929).

[*] Personal communication, August 1939; see also, R. T. Birge, *Phys. Rev.*, **58**, 658 (1940) and the Appendix to this volume.

[2] *Rev. Mod. Phys.*, **11**, 65 (1939).

[3] *J. Res. Nat. Bur. Stand.*, **22**, 375 (1939).

PART I—QUANTUM PHENOMENA

1. SPECTRAL TERMS AND CRITICAL POTENTIALS

(1) Series Relations for Spectral Lines: * While an incandescent solid body emits a *continuous* spectrum, that is a spectrum in which the energy in any range between λ (the wave length) and λ + dλ is a continuous function of λ, the radiation from gases and vapors consists either of sharply defined lines (*line spectra*), or bands which extend over certain ranges of wave lengths (*band spectra*). The latter are characteristic of diatomic and polyatomic molecules, while the former are due to excitation of atoms. Both these types of spectra are observed in an electrical discharge in hydrogen, the band spectrum being due to the presence of the molecules, while the line spectrum occurs because of the presence of atoms formed by dissociation of the molecules. In the case of sodium and mercury vapor, the spectrum consists ordinarily of a series of discrete lines, and since the time of Kirchhoff and Bunsen it has been recognized that each element possesses a characteristic line spectrum. This observation has been applied, as is well known, to the identification of the various elements in spectroscopic methods of analysis.

The very existence of line spectra led physicists to conclude that the structure of the atom must be quite complex in order to give rise to such spectra. It was only, however, with the discovery of the existence of certain interesting relations among the lines of any one element that the foundations were laid for our present views on atomic structure. In 1885 Balmer[1] pointed out that in the ordinary spectrum of (atomic) hydrogen there exists an interesting relation
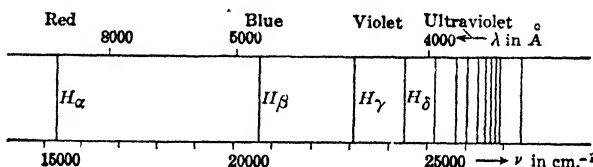

FIG. 1.1.   Spectrum of Balmer Series

between the different lines. This spectrum (see Fig. 1.1) consists of a series of lines known as H_α, H_β, H_γ, H_δ, etc., extending from the red into the ultra-

* This topic is discussed comprehensively in the following treatises:

F. K. Richtmeyer, Introduction to Modern Physics, 2nd Ed., Chapter X. McGraw-Hill Book Co., Inc. New York. 1934. (Ref. F. K. R.)

H. E. White, Introduction to Atomic Spectra, Chapter I. McGraw-Hill Book Co., Inc., New York, 1934. (Ref. H. E. W.)

A. C. Candler, Atomic Spectra and the Vector Model, Volume I, Series Spectra. University Press, Cambridge, 1937. (Ref. A. C. C.)

The early observations and systems of classification as well as the different notations have also been discussed very fully by R. C. Gibbs, *Rev. Mod. Phys.*, **4**, 278 (1932). This report contains a bibliography of papers published during 1920–1931 on the spectra of the different elements.

[1] *Ann. Physik*, **25**, 80 (1885).

violet region. R. W. Wood [1] has been able to obtain photographs of this spectrum as far as the 20th line, while in photographs of nebular clusters the series have been obtained as far as the 33rd line. Balmer observed that the wave length of each of the lines of the series (then known) could be represented satisfactorily by the formula

$$\lambda = A \frac{m^2}{m^2 - 4}, \qquad (1.1)$$

where λ denotes the wave length, m has the values 3, 4, 5, 6 for H_α, H_β, H_γ, H_δ, respectively, and A is a constant.

The formula is more usually written in the form

$$\bar{\nu} = \frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{m^2}\right), \qquad (1.2a)$$

where $R = 109{,}677.76$ cm.$^{-1}$ is known as the *Rydberg constant*, $m = 3, 4, 5, 6$, etc., and $\bar{\nu}$ is known as the *wave number*.[*]

"This relation gives with an accuracy of one part in 100,000 the frequencies not only of the four lines discussed by Balmer [**]

H_α,	$\lambda = 6562.8$ Å,	$\bar{\nu} = 15{,}233.0$ cm.$^{-1}$
H_β,	4861.3	20,564.6
H_γ,	4340.5	23,032.3
H_δ,	4101.7	24,372.8

but also all of the other observed lines in the Balmer series." [2]

Equation (1.2a) may also be written in terms of the frequency in the form

$$\nu = \frac{c}{\lambda} = Rc\left(\frac{1}{2^2} - \frac{1}{m^2}\right), \qquad (1.2b)$$

where $c =$ velocity of light $= 2.99776 \times 10^{10}$ cm. sec.$^{-1}$. From this equation it will be observed that *Balmer's formula expresses the frequency of a line in the spectrum of hydrogen as the difference between a constant term $Rc/2^2$ and a variable term Rc/m^2*. Putting $m = \infty$, we obtain the *limiting frequency* or *head* of the series, corresponding to $\bar{\nu} = R/4$. This is represented in Fig. 1.1 by the line on the extreme right.

---

[1] R. W. Wood, *Proc. Roy. Soc.*, [A], 97, 455 (1920).

[*] This method for distinguishing between *wave number* and *frequency* has been used by A. E. Ruark and H. C. Urey, Atoms, Molecules and Quanta, McGraw-Hill, 1930.

[**] In the case of optical spectra wave lengths are usually expressed in terms of Angstroms (Å) where Å $= 10^{-8}$ cm. In the past it has also been customary to use the micron (1 μ $= 10^{-4}$ cm. $= 10^{-6}$ meter) and millimicron (1 mμ $= 10^{-7}$ cm.). The micron is a convenient unit in the case of infra-red spectra.

[2] L. Pauling and S. Goudsmit, The Structure of Line Spectra, p. 3. McGraw-Hill Book Company Inc., New York, 1930. (Ref. P. G.)

Before discussing the investigations of Rydberg (1890) which followed that of Balmer, mention should be made of other series in the spectrum of atomic hydrogen which have been discovered since the earlier work.

In 1909 Paschen found a series in the infra-red region for which the wave numbers could be expressed by the relation

$$\tilde{\nu} = R\left(\frac{1}{3^2} - \frac{1}{m^2}\right) \tag{1.3}$$

with the same value of R as that given by Balmer's relation.
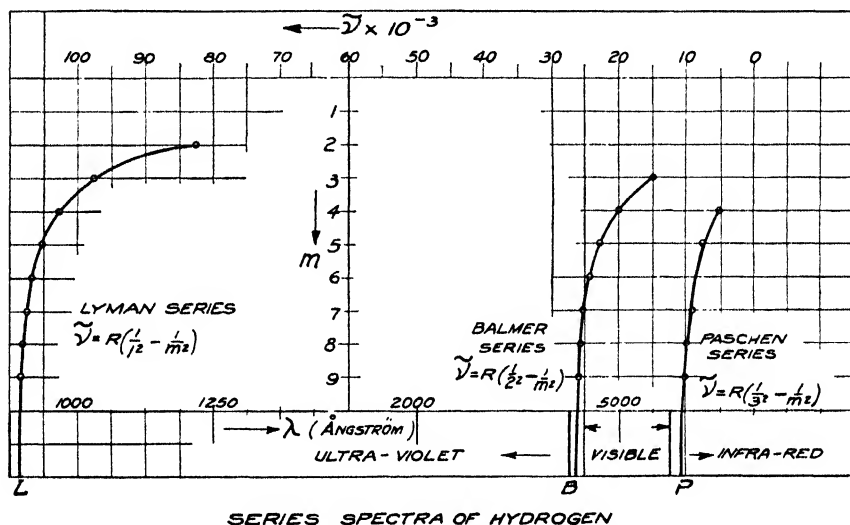

SERIES SPECTRA OF HYDROGEN

FIG. 1.2.   Series Spectra of Hydrogen, Showing Wave Numbers Corresponding to Different Values of m

Also, Lyman (1904, 1906) observed a series in the ultra-violet corresponding to the relation

$$\tilde{\nu} = R\left(\frac{1}{1^2} - \frac{1}{m^2}\right). \tag{1.4}$$

More recently Brackett [1] discovered a series still further in the infra-red corresponding to

$$\tilde{\nu} = R\left(\frac{1}{4^2} - \frac{1}{m^2}\right) \tag{1.5}$$

and Pfund [2] observed two members of the series whose limit is $R/5^2$. Since then Poetker [3] has found other members of this series of still longer wave length.

[1] F. S. Brackett, *Astrophys. J.*, **56**, 154 (1922).

[2] A. H. Pfund, *J. Opt. Soc. Am.*, **9**, 193 (1924).

[3] A. H. Poetker, *Nature*, **119**, 123 (1927); *Proc. Roy. Soc.*, [A], **30**, 418 (1927).

Each of these series may be expressed by an equation of the type

$$\nu = Rc\left(\frac{1}{n^2} - \frac{1}{m^2}\right),\tag{1.6}$$

in which m and n are integers, with $m \geqslant n + 1$, and Rc/n^2 is the *limit* of the series.

Figure 1.2 shows graphs for the series in which the value of the wave number, $\bar{\nu}$, *for each line* is plotted against the corresponding value of m. The limit for each series ($\bar{\nu}$ for $m = \infty$) is represented by the line to the left of each curve, which corresponds to one of the terms in equation (1.6).
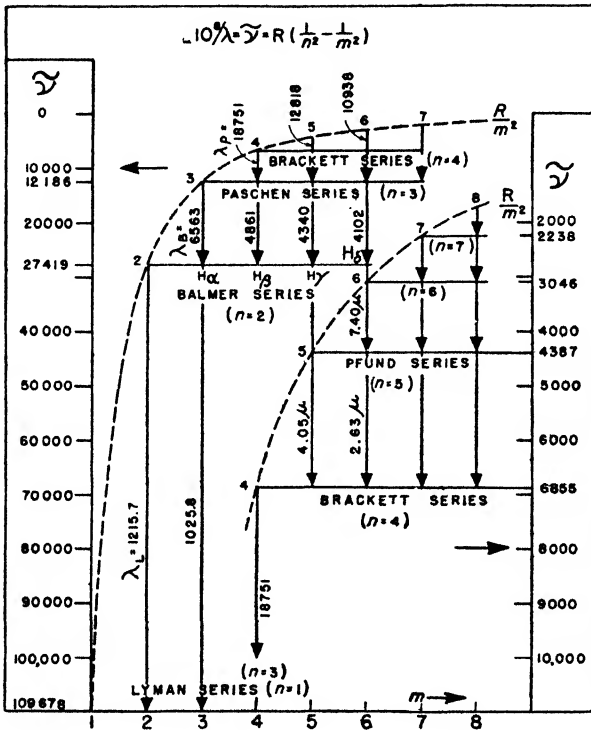

FIG. 1.3. Plot of R/m^2 versus m, Illustrating the Relation Between Wave Numbers of Spectral Lines and Those of the Associated Terms

If we plot these limiting wave numbers or *spectral terms* against m as abscissa, we obtain the curve shown in Fig. 1.3. It will be observed that each of the vertical lines marked with an arrow corresponds to a first member of the series for which the lower term is the limit. Thus λ_L is the first member of the

Lyman series, i.e.,

$$\bar{\nu} = \frac{1}{\lambda} = R \left(\frac{1}{1^2} - \frac{1}{2^2} \right),$$

while λ_B and λ_P represent first members of the Balmer and Paschen series respectively.

If we multiply each side in equation (1.6) by Planck's constant, we obtain the *energy relation*,

$$h\nu = Rch \left(\frac{1}{n^2} - \frac{1}{m^2} \right), \tag{1.7}$$

which, on the basis of Planck's theory, leads to the conclusion that the emission of the *energy quantum hν* corresponds to a *transition of the atomic system from a state of higher to one of lower energy*. Apart from an additive constant, these energy states correspond to the values,

$$E_n = - \frac{Rch}{n^2} \qquad \text{and} \qquad E_m = - \frac{Rch}{m^2},$$

where the emitted radiation is given by the relation

$$\nu = \frac{1}{h} (E_m - E_n). \tag{1.8}$$

That is, the *spectral terms derived from a study of the line spectra correspond to different possible energy states of the atomic system*.

It was considerations of this nature that led Bohr to his theory of the origin of spectral lines and the nature of atomic structure. Before, however, describing this theory and some of the deductions from it, it is necessary to resume the discussion of the investigations which followed the remarkable suggestion by Balmer.

In 1890 Rydberg showed that for a number of elements (those of the alkali and alkaline earth groups) the spectral lines can be classified into a number of different series, for each of which there exists a relation similar to Balmer's of the form

$$\bar{\nu}_m = \bar{\nu}_\infty - \frac{R}{(m + \alpha)^2}, \tag{1.9}$$

where the value of R is approximately identical with that deduced by Balmer,[1]

[1] The differences in values of R for different elements are quite small. Thus according to R. T. Birge (*Phys. Rev.* (Supplement), **1**, 60 (1929)) the values for hydrogen and helium are as follows:

$$R_H = 109,677.759 \text{ cm.}^{-1}; \qquad R_{He} = 109,722.40 \text{ cm.}^{-1}.$$

According to the Bohr theory the Rydberg constant for any element is given by

$$R = R_\infty \Big/ \left(1 + \frac{m}{M} \right),$$

where m = mass of electron, M = mass of atom. Hence R_∞ = Rydberg constant for infinite mass, and from the values for R_H and R_{He}, it follows that $R_\infty = 109,737.45 \text{ cm.}^{-1}$.

while m is an integer whose value increases from 1 or 2 by unity for each successive member of the series in order of decreasing wave length (increasing wave number). For any one series $\bar{\nu}_\infty$ (the *limit* or *convergence* of the series) and α are characteristic constants.

Thus in the case of sodium (and other metals of the same group) the spectral lines can be arranged in four series which are designated as follows:

Principal:
$$\frac{1}{\lambda} = R\left[\frac{1}{(1+s)^2} - \frac{1}{(m+p)^2}\right], \quad m = 2, 3 \ldots$$

Sharp:
$$\frac{1}{\lambda} = R\left[\frac{1}{(2+p)^2} - \frac{1}{(m+s)^2}\right], \quad m = 2, 3 \ldots$$

Diffuse:
$$\frac{1}{\lambda} = R\left[\frac{1}{(2+p)^2} - \frac{1}{(m+d)^2}\right], \quad m = 3, 4 \ldots$$

Fundamental:
$$\frac{1}{\lambda} = R\left[\frac{1}{(3+d)^2} - \frac{1}{(m+f)^2}\right], \quad m = 4, 5 \ldots$$

In these formulae, s, p, d and f designate the particular values of the constant α of equation (1.9) for each series of terms.

A further investigation of the spectra of the alkali elements shows that the terms involving p, d and f are actually doublets. Thus the two D-lines of sodium, $\lambda 5896$ and $\lambda 5890$, which constitute the first members of the principal series, correspond to two terms of the form $R/(1+p_1)^2$ and $R/(1+p_2)^2$, with the term involving s common to both lines. For the sodium D-lines the value of $\Delta\bar{\nu}$, the separation of the doublet, is 17.18 cm.$^{-1}$ and for higher members of the series this separation decreases continuously.

In the case of the elements of the second group it has been found that the spectral lines can be classified into two groups in one of which the lines are singlets and in the other triplets. Furthermore, in each of these groups the lines can be arranged in four series as in the case of the alkali elements.

As we pass in the periodic arrangement to Group III (the B-Al group) and groups more to the right, the maximum attainable number of multiplets, analogous to the doublet terms in the case of Na, increases, so that for an element such as Mn the number of multiplets observed may be as high as eight. It is the existence of these multiplet terms in the spectra of elements of Groups III to VIII that made it difficult, for a long time, to arrange their spectra in series. In fact, it was only after Bohr had announced his theory of the origin of spectral lines that methods were developed, suggested by this theory, by which these more complicated spectra could be investigated successfully for the determination of the corresponding terms.

It will be observed that in the case of the sharp series for Na, the limit of this series is the first term in the principal series. Similarly the limit of the fundamental series is the first term in the diffuse series. In the case of the spectrum of mercury, lines are observed which are due to combination of

singlet and triplet terms. These are known as *intercombination lines.* These observations illustrate a general law, discovered by Rydberg and Ritz, known as the *Principle of Combination*, which states the possibility of the occurrence of spectral lines as a result of the combination of terms in different series. Actually not all such possible combinations are observed because of the existence of selection rules (see subsequent discussion), according to which certain transitions between terms are forbidden.

(2) **Bohr Theory of Energy Levels:** As mentioned in the previous section, these observations made by Balmer and Rydberg, when combined with the concept of energy quanta of magnitude $h\nu$, lead to the view that the spectral lines arise from transitions of an atomic system from states of higher to those of lower energy. This deduction which has been stated already in the form of equations (1.7) and (1.8) is essentially the fundamental idea in Bohr's theory.[1]

It is well to point out that in suggesting this theory of the origin of spectral lines Bohr modified Planck's original hypothesis quite radically. For according to Planck's original theory, which followed in some respects the classical ideas on the mechanism by which electromagnetic waves are radiated, the energy quantum is emitted or absorbed by an *oscillator* (electric doublet) having the *same frequency* of vibration as that of the radiation. That is, according to Planck's original suggestion, the change in energy, ΔE is determined by the frequency of an oscillator and is identical with the latter, according to the relation,

$$\Delta E = h\nu = h\omega,$$

where ν is the frequency of the radiation and ω that of the oscillator.

This point of view was completely discarded by Bohr, and instead he postulated the relation

$$\nu = \Delta E/h,$$

that is, the *frequency of radiation emitted or absorbed by an atomic system is determined only by the magnitude of the change in total energy.*

"If this law is assumed," Bohr states,[2] "the spectra do not give us information about the motion of the particles in the atom as is supposed in the usual theory of radiation, but only a knowledge of the energy changes in the various processes which can occur in the atom. *From this point of view the spectra show the existence of certain definite energy values corresponding to certain distinctive states of the atoms.* These states will be called the *stationary states* of the atoms, since we shall assume that the atom can remain a finite time in each state, and can leave this state only by a process of transition to another stationary state."

Bohr's assumptions on which he bases his theory of spectral series have been stated by him in the following form.[3]

[1] *Phil. Mag.*, **26**, 1, 476 (1913).

[2] N. Bohr, The Theory of Spectra and Atomic Constitution, p. 23, Cambridge Univ. Press, 1922.

[3] N. Bohr, On the Quantum Theory of Line Spectra, Copenhagen (1918). Part I, p. 5.

Postulate A: "An atomic system can, and can only, exist permanently in a certain series of states corresponding to a discontinuous series of values for its energy, and consequently any change of the energy of the system, including emission and absorption of electromagnetic radiation, must take place by a complete transition between two such states. These states will be denoted as the 'stationary states' of the system."

Postulate B: That the radiation absorbed or emitted during a transition between two stationary states is monochromatic and possesses a frequency ν, given by the relation

$$h\nu = E_m - E_n. \tag{1.10}$$

Let us consider from this point of view the significance of the series of spectral terms observed for atomic hydrogen. The line corresponding to the limit of the Lyman series, that is the line defined by the value $\tilde{\nu} = R = 109{,}678$ cm.$^{-1}$, represents the highest frequency and therefore the maximum value of $h\nu$ emitted by a transition from any of the upper energy states to that of lowest energy. The latter must evidently correspond to the normal or unexcited state of the hydrogen atom, while all the upper states arise from excitation of the atom through some external source of energy. This energy may be supplied by collisions of the atoms with electrons in an electrical discharge. While Bohr actually developed a model of these "excited states" in terms of electronic orbits, it is not essential, in the present connection, to discuss the details of this model. For the most important aspect of Bohr's theory is his interpretation of spectral terms as "stationary states." In other words, the spectral terms, as derived from a study of the line spectrum of an atomic system, give us information on the sequence of these states and their relative energy values.

Now it is evident that in the case of hydrogen, the highest possible state of excitation is that associated with the limit of the Lyman series, which we shall designate as $\tilde{\nu}_\infty$. If the corresponding amount of energy, $h\tilde{\nu}_\infty c$, is imparted to a normal hydrogen atom it becomes ionized, that is, the electron is completely removed from the atom.* We can therefore regard the energy $h\tilde{\nu}_\infty c$ as a measure of the *energy of binding* between the electron and the positively charged residue (which in the case of hydrogen is a proton).

Similarly it is observed that in the case of other atomic systems, such as Na and Hg, the stationary state corresponding to the highest value for $\tilde{\nu}_\infty$, the limit of any of the spectral series, represents the minimum energy for the ionization of the atom.

If therefore we regard energy that is emitted as positive, then the normal or unexcited state must be one of *negative energy* as compared with any of the excited states. Evidently the simplest procedure is to assume that the *ionized state corresponds to the zero of the energy scale*, in which case the energy for the normal or lowest state has the value, $E = -h\tilde{\nu}_\infty c$.

---

* This identification of the limit of the series with the ionization energy is confirmed by experimental observations, as mentioned below.

Thus the energy of the normal state for H is

$$E = - hR_{\mathrm{H}}c$$
$$= - 6.624 \times 10^{-27} \times 109{,}678 \times 2.9976 \times 10^{10}$$
$$= - 2.178 \times 10^{-11} \text{ erg,}$$

while the successive stationary states have the energies $- hR_{\mathrm{H}}c/4$, $- hR_{\mathrm{H}}c/9$, and so forth.
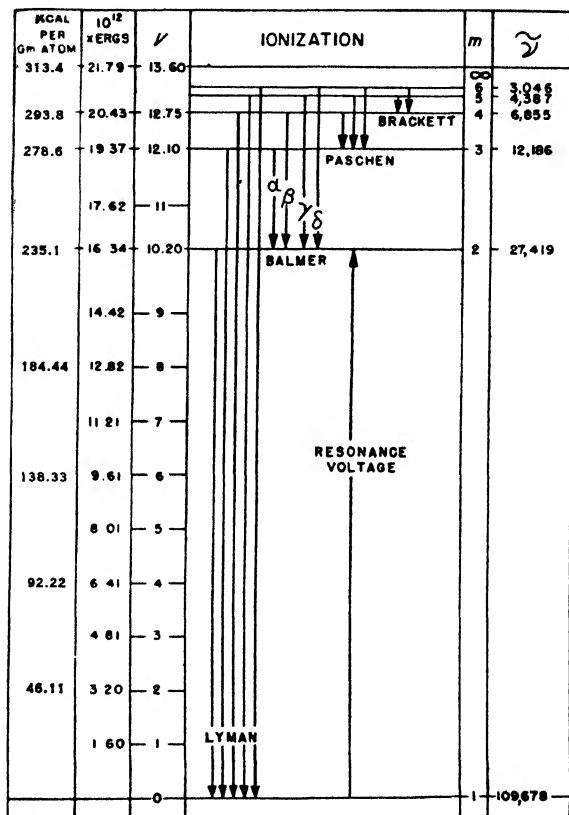

FIG. 1.4.   Energy Level Diagram for Atomic Hydrogen

In this manner we obtain the *energy level* diagram shown in Fig. 1.4, in which the transitions corresponding to the different spectral lines are shown as vertical lines with arrows. The value of the energy may be expressed in terms of calories per gm-atom, by means of the conversion factor

$$\text{cal. gm.-atom}^{-1} = \text{erg atom}^{-1} \cdot \frac{N}{10^7 \times J_{15}} = 1.439 \times 10^{16} \text{ erg atom}^{-1}$$

where

$$N = \text{Avogadro's constant} = 6.0227 \times 10^{23} \text{ mole.}^{-1}$$
$$J_{15} = \text{Mechanical equivalent of heat}$$
$$= 4.1847 \text{ abs. joule cal.}_{15}^{-1}.$$

Thus the energy required to excite a normal hydrogen atom to the state of zero energy is equal to 313,400 cal. gm.-atom^{-1}: this is approximately three times the heat of dissociation of H_2 (102,700 cal. mole^{-1}).

For reasons, which will become apparent after the discussion in the following sections, it is customary in the case of energy levels of atomic systems to express the energy in terms of *electron volts* (e.v.). An electron, of charge e, accelerated through a potential difference of V volts acquires a kinetic energy given by the relation

$$E = \tfrac{1}{2} mv^2 = Ve.10^8/c \qquad (1.11)$$
$$= 1.6019 \times 10^{-12} V \text{ erg,}$$

where
$$m = \text{mass of electron (gm.),}$$
$$v = \text{velocity (cm. sec.}^{-1}),$$

and $10^8/c$ is the factor required to convert absolute volts to electrostatic units. Thus to excite H to the zero energy state (the ionization potential) requires $(2.178 \times 10/1.6019 =)$ 13.595 electron volts.*

Figures 1 5 and 1.6 show energy level diagrams for sodium and mercury respectively as deduced from a study of the spectral lines. Similar diagrams are now available for a large number of elements.[1]

In this connection it is also necessary to make some remarks regarding the notation used to designate spectral terms.[2] Evidently it is necessary to indicate, with respect to any term the series of which it is a member and the order in which it occurs in the series. During the development of spectroscopy previously to about 1920, various systems of notation were used.[3] However,

---

* It is also convenient to note the following conversion factors: $\dfrac{Ne.10^8}{J_{15}c} = 23{,}055$ cal. mole^{-1} abs.-volt^{-1}. Energy associated with unit wave number, $E/\bar{\nu} = hc = 1.9856 \times 10^{-16}$ erg cm Wave number associated with unit abs.-volt, $\bar{\nu}/V = 8067.7$ cm.$^{-1}$ abs.-volt^{-1}. Wave length associated with unit abs.-volt, $\lambda = hc^2/e = 12{,}395 \times 10^{-8}$ cm. abs.-volt. Energy per mole associated with unit frequency, $E/\nu = \dfrac{Nh}{10^7.J_{15}} = 9.533 \times 10^{-11}$ cal. sec. mole^{-1}.

[1] W. Grotrian, Graphische Darstellung der Spektren, Two volumes, Julius Springer, Berlin (1928).

R. F. Bacher and S. Goudsmit, Atomic Energy States, McGraw-Hill Book Company (1932). (Ref. B. G.) This gives values of the spectral terms for a very large number of elements, from which energy level diagrams may be readily plotted. See also Refs. H E. W. and A. C. C.

[2] Further details will be given in a subsequent section.

[3] See Refs. F. K. R., and H. E. W.

at the present time, it has become common practice to refer to the different series thus:

Sharp series	S
Principal series	P
Diffuse series	D
Fundamental series	F

FIG. 1.5.   Energy Level Diagram for Sodium

In the case of elements of higher valence, other series have been observed which are designated similarly by the letters G, H, etc.   A prefix at the upper left-hand corner of the series symbol indicates the degree of multiplicity.   For instance, ^1P and ^3D signify terms in the singlet P series and triplet D series respectively.

The order of the terms in a series is indicated by an integer. Formerly the number 1 or 2 was used for the lowest term and this was increased by unity for each successively higher term. This is followed to some extent even now, but in the case of the alkalis and alkaline earth elements it is usual to assign
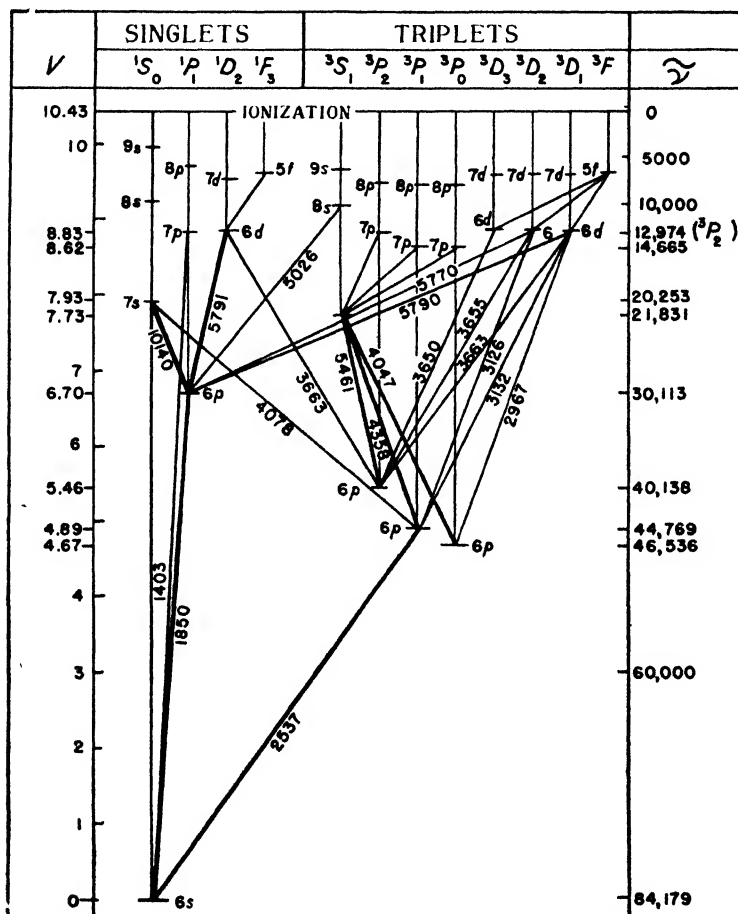

FIG. 1.6. Energy Level Diagram for Mercury

to the lowest term the corresponding total quantum number, n, of the valence electron. Also it is customary to add a suffix at the lower right hand corner of the series symbol, which serves to distinguish the different members of a multiplet term and is designated the inner quantum number. (The significance of these quantum numbers will be discussed in a subsequent section.)

In accordance with this notation the spectral lines of the different series in sodium, for example, are represented as follows:

Principal series:	$n^2P_{1/2} - 3^2S_{1/2},$	$n^2P_{3/2} - 3^2S_{1/2};$
Sharp series:	$n^2S_{1/2} - 3^2P_{1/2};$	$n^2S_{1/2} - 3^2P_{3/2};$
Diffuse series: *	$n^2D_{5/2} - 3^2P_{3/2};$	$n^2D_{3/2} - 3^2P_{1/2};$
		$n^2D_{3/2} - 3^2P_{3/2};$
Fundamental series:	$n^2F_{7/2} - 3^2D_{5/2};$	$n^2F_{5/2} - 3^2D_{3/2};$
		$n^2F_{5/2} - 3^2D_{5/2}.$

In these series $n \geqslant 4$, and it will be observed that the limit of each series constitutes the second term.

Similarly the lines λ2537 and λ5461 in the spectrum of mercury are represented by the notations

$$6^3P_1 - 6^1S_0 \qquad \text{and} \qquad 7^3S_1 - 6^3P_2 \text{ respectively.}$$

(3) **Absorption Spectra and Resonance Lines:** If the D-lines of sodium as obtained from a sodium vapor electric discharge lamp are viewed through sodium vapor at a sufficiently high temperature (300° C. approximately) the two lines appear dark.[1] That is, sodium vapor absorbs radiation of these wave lengths. A similar observation may be made with a low pressure mercury vapor lamp, which is a very efficient source of the ultra-violet line λ2537. This radiation may be detected either by means of a sodium photo-tube or by the fluorescence produced on a plate coated with a suitable material such as willemite. If now a stream of mercury vapor (the vapor pressure of mercury at room temperature is sufficiently high to produce the effect), is passed between the source of radiation and the detector, the latter shows that the line λ2537 has been absorbed. The Fraunhofer lines, observed as dark lines on the continuous background of the solar spectrum, have been interpreted in a similar manner as absorption lines due to the presence of different elements in the sun's outer atmosphere.

On the basis of Bohr's theory of energy levels the explanation of these observations is obvious. Since the D-lines of sodium, as shown in Fig. 1.5, are due to a transition from the lowest excited states ($3P_{3/2}$ and $3P_{1/2}$) to the normal ($3S$) state, it follows that sodium atoms in the normal state absorb this radiation and are thereby excited to the $3P$ states. The interesting point to note is that radiation of lower frequency is not absorbed, nor is radiation of higher frequency than that of the D-lines, unless this frequency coincides with that of a transition between one of the higher excited states in Na and the lowest

---

* It will be observed that in the diffuse and fundamental series there are actually present three components for a given value of n. However, the separation between two of these is usually so small that it can be observed only under very high resolving power.

[1] Apparatus for observations on the absorption of light by sodium vapor has been described by D. C. Stockbarger, *J. Opt. Soc. Am.*, **30**, 362 (1940).

state. Actually Wood and Fortrat [1] found that in a long column of sodium vapor they obtained in absorption 58 lines of the principal series $m^2P - 3^2S$. Similarly, by absorption of $\lambda 2537$, mercury atoms are excited (as is seen from Fig. 1.6) from the normal to the 6^3P_1 state. Evidently the measurement of characteristic absorption lines may be used to determine the energy of the ground or normal level with respect to the level from which the corresponding lines originate. However, as will be pointed out in another connection, it is also possible under certain conditions to obtain absorption of lines which correspond to transitions from excited states. Thus, if the gas or vapor is at a high temperature, as in stellar atmospheres, or electrically excited, there may be a sufficiently high concentration of atoms in excited states to absorb monochromatic radiations of such frequencies as will excite them to still higher energy states.

Because of the similarity to the resonance phenomena observed with electromagnetic waves these lines which correspond to transitions from the normal to the next higher excited states are known as *resonance lines*. In the period immediately following the publication of Bohr's papers the subject of line absorption spectra received considerable attention,[2] since such observations led not only to determinations of the wave numbers for the normal energy states but also to some very interesting conclusions regarding the "life" of excited states—a topic which is discussed more fully towards the end of this chapter.

While the theory of energy levels and Bohr's concept of energy emission and absorption in units of magnitude $h\nu$ gave a better interpretation of observations on absorption of spectral lines, even more direct evidence for this new point of view was obtained through a series of investigations initiated by Franck and Hertz.

(4) **Critical Potentials:** Bohr's concept of the existence of discrete energy levels suggested to J. Franck and G. Hertz [3] a method for the determination of these levels which has not only served to confirm the validity of the theory but has also proved useful in supplementing the information deduced from spectroscopic observations.

The method consists essentially in bombarding atoms of the vapor or gas by electrons having a definitely known kinetic energy. The gas or vapor is at such a low pressure that the electrons can make at the most only one collision in passing from the cathode to a positively charged grid. For electrons starting from a thermionic cathode (so that the initial velocity is negligible) and suffering no collisions, the velocity v acquired on reaching the grid is given by the relation

$$E = \tfrac{1}{2} mv^2 = Ve.$$

[1] *Astrophys. J.*, **43**, 73 (1916).

[2] P. D. Foote and F. L. Mohler, The Origin of Spectra, The Chemical Catalog Company, Inc. New York, 1922. (Ref. F. M.)

[3] *Verh. Deutsch. Physik. Ges.* **16**, 512 (1914); *Physik. Z.*, **17**, 409 (1916).

Expressing V in volts,* the energy in ergs is given by equation (1.11), that is,

$$E = 1.6019 \times 10^{-12} \, V \text{ erg}$$

and the velocity of the electrons, by the relation

$$v = \sqrt{2.10^8(e/m)V}$$
$$= 5.9314 \times 10^7 \sqrt{V} \text{ cm. sec.}^{-1}. \tag{1.12}$$

Now let us consider what happens as the kinetic energy of the electrons is increased from zero. In the case of Na vapor, no radiation is observed until the energy is increased to 2.10 volts, but at this point the emission of the D lines is observed. The interpretation is that the electrons have given up this energy in exciting some of the atoms to the $3P$ state in accordance with the relation

$$E = Ve = h\nu = hc\Delta\tilde{\nu}, \tag{1.13a}$$

where $\Delta\tilde{\nu}$ is the difference in the wave numbers of the normal ($3S$) and $3P$ levels, and ν is the frequency of the emitted radiation.

To obtain the relation between V in absolute volts and the wave number difference in cm.$^{-1}$, it is necessary to express the potential in e.s.u., and consequently equation (1.13a) assumes the form,

$$V = c^2 \cdot 10^{-8} \cdot \frac{h}{e} \Delta\tilde{\nu}$$
$$= \Delta\tilde{\nu}/(8067.7) = 1.2395 \times 10^{-4}\Delta\tilde{\nu}. \tag{1.13b}$$

Since the values of $\tilde{\nu}$ for the $3S$ and $3P_{1/2}$ levels in the case of Na, are 41,449 cm.$^{-1}$ and 24,493 cm.$^{-1}$ respectively, $\Delta\tilde{\nu} = 16,956$, and it follows from the last equation that $V = 2.10$ volts, as observed.

At accelerating potentials below this value, the electrons suffer only *elastic* collisions with Na atoms. On the basis of ordinary dynamics it may be shown that the loss in energy of the electrons is $(2m/M)E$, where m/M denotes the ratio of the mass of the electron to that of the atom. For sodium,

$$\frac{2m}{M} = \frac{2}{1837.5 \times 23} = 4.73 \times 10^{-5},$$

and the loss of energy is therefore negligible.

When the energy of the electrons exceeds 2.10 volts, *inelastic* collisions occur, because of the excitation of Na atoms to the $3P$ state, and then as the latter return *spontaneously* to the normal state the additional energy is emitted in the form of monochromatic radiation of frequency

$$\nu = \Delta E/h = Ve/h.$$

---

* The term volts is used in this chapter as synonymous with absolute volts.

In terms of wave length of the emitted line, this relation takes the form,

$$\lambda = \frac{c}{\nu} = \frac{ch}{Ve}. \qquad (1.14)$$

For V expressed in volts,

$$\lambda = 12{,}395 \times 10^{-8}/V \text{ cm.}$$

which is equivalent to equation (1.13b).

As the electron voltage is increased beyond 2.10 volts, no other lines appear until the value 3.18 volts is reached at which point additional lines are emitted due to excitation of the sodium atom to the $4S$ level. These have the wave lengths $\lambda 11382$ and $\lambda 11404$ and are in the infra-red region. As the kinetic energy of the electrons is increased still more, other lines in the visible region appear until finally, for $V = 5.14$ volts or higher,* *all* the lines in the arc spectrum of Na are brought out. At this potential the Na atom loses its valence electron and becomes a Na^+ ion. Thus the complete arc spectrum of sodium is obtained only at voltages exceeding the so-called *ionization potential*, which as mentioned already, corresponds to the state of zero energy. On the other hand, if the electron velocity is maintained at a value just above that corresponding to the first excited, or *resonance*, state only a single line spectrum is emitted (which of course may actually be a close doublet or triplet). In the decade following the publication of Franck and Hertz's paper the investigation of single line spectra formed a very useful method for the determination of resonance potentials.[1]

Figure 1.7a taken from a paper by J. A. Eldridge[2] shows the mercury spectrum at 8.7 and 9.7 volts, while Fig. 1.7b shows similar observations for helium taken at 23.6 and 24.4 volts by G. Hertz.[3]

These observations are in agreement with the conclusions to be drawn from the energy level diagrams for the two elements as shown in Figs. 1.6 and 15.2 (see page 307). Those voltages at which new lines appear and which from the point of view of Bohr's theory correspond to stationary states of the atomic system are known as *critical potentials*. It follows that the potentials for ionization (V_i) and for resonance (V_r) are merely two of these potential values which are of special importance. Furthermore, if we indicate by $\tilde{\nu}_X$ and $\tilde{\nu}_N$ the wave numbers for any excited state and the normal state respectively, it follows from the preceding relations that the critical potential (V_c) corresponding to the line of wave number $\tilde{\nu}_N - \tilde{\nu}_X$ is given by equations (1.13b), that is,

$$V_c = \frac{\tilde{\nu}_N - \tilde{\nu}_X}{8067.7} \text{ volts.}$$

* Since $\tilde{\nu}_\infty = 41{,}449$, $V = 5.138$.

[1] Illustrations of such single line spectra are given by F. M. *op. cit.*, pp. 128–9.

[2] *Phys. Rev.*, **23**, 685 (1924).

[3] *Z. Physik*, **22**, 18 (1924). These two spectrograms (based on photographs) are taken from the Nobel address by G. Hertz, Stockholm (1927).

In Figs. 1.7a and 1.7b, the value of V_c corresponding to each line is indicated beside the value of λ for the line.*
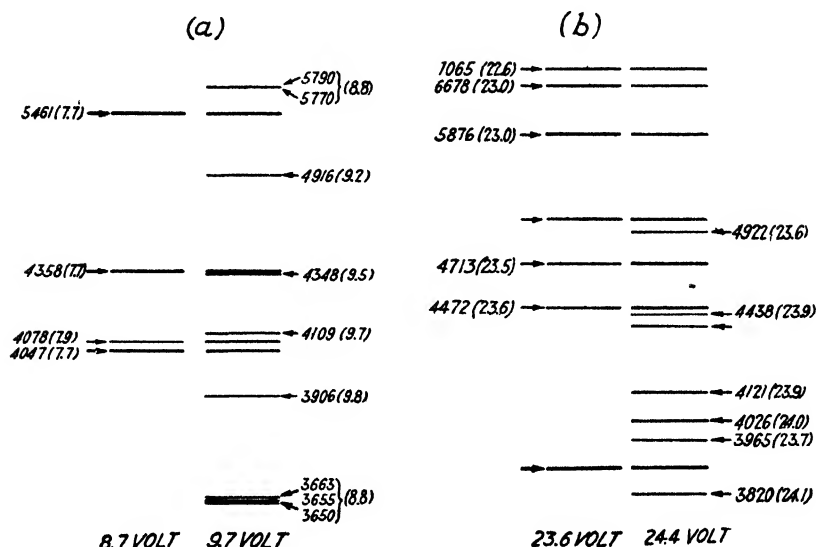

FIG. 1.7(a) and (b).   Spectra of Mercury (a) and Helium (b) for Different Velocities of Bombarding Electrons

A number of other methods have also been used for the determination of critical potentials.   Typical is the one used by Franck and Hertz[1] in which the electrons from a hot cathode are accelerated by means of a positive voltage applied to a grid situated between a plate and the cathode.   If the electrons have lost energy by inelastic collision they are prevented from reaching the plate by a small retarding potential.   In consequence the current to the plate exhibits a maximum at each critical potential.   The plot in Fig. 1.8, obtained by Tate and Foote[2] shows data obtained in this manner for sodium vapor.
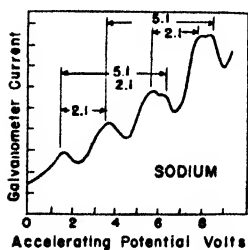

FIG. 1.8.   Critical Potential Curve for Sodium.

Other methods are fully described in the report on "Critical Potentials" by K. T. Compton and F. L. Mohler,[3] in the trea-

* These values were calculated by means of the relation $V_c = \Delta \bar{\nu}/8106$, which was based on the 1930 values of h and e.

[1] *Loc. cit.*   An excellent description of this method is given by G. P. Harnwell and J. J. Livingood, Experimental Atomic Physics, McGraw-Hill (1933), p. 314 et seq. (Ref. H. L.)

[2] *J. Wash. Acad. Sci.*, 7, 517 (1917).   The figure is actually taken from H. E. W., p. 94.

[3] *Bull. Nat. Res. Council*, 9, Part 1 (1924).

tise by J. Franck and P. Jordan,[1] and in papers by H. Kallman and B. Rosen [2] and H. D. Smyth.[3]
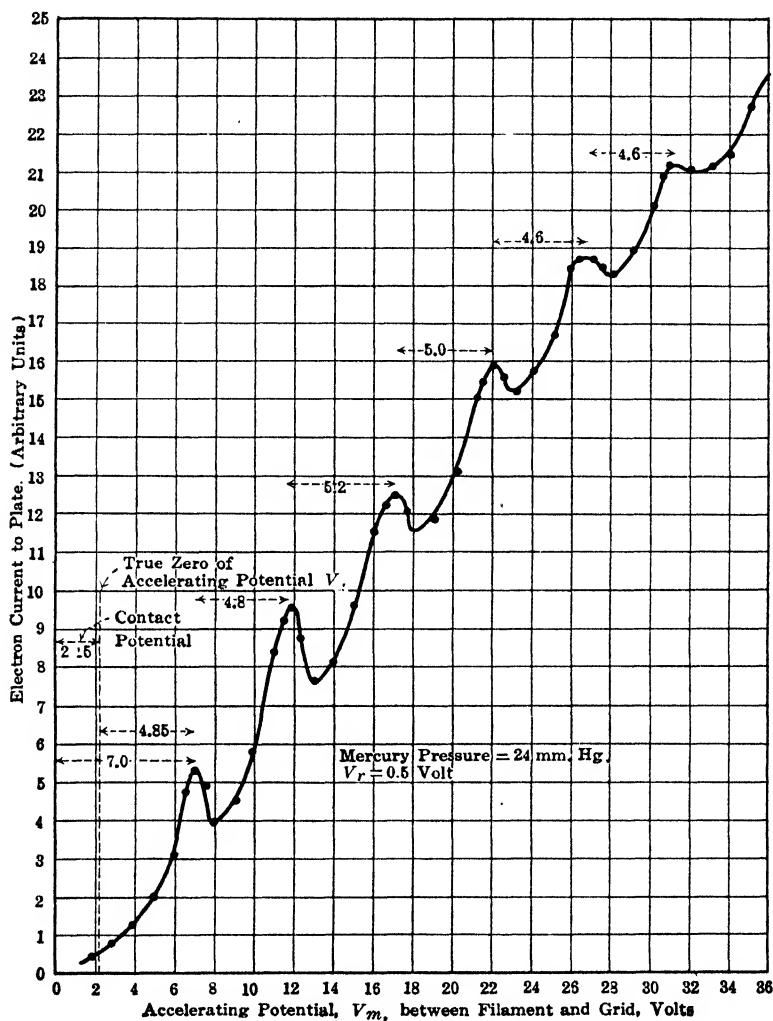

FIG. 1.9. Inelastic Impact Curve Obtained for Mercury.

Laboratory methods for the determination of critical potentials have been described by G. P. Harnwell and J. J. Livingood,[4] from which Fig. 1.9 is taken,

[1] Anregung von Quantensprüngen durch Stösse, Julius Springer, Berlin (1926).
[2] *Physik. Z.*, **32**, 521 (1931).
[3] *Rev. Mod. Phys.*, **3**, 347 (1931).
[4] Ref. H. L., p. 317.

this shows an inelastic impact curve obtained for mercury vapor in a three-electrode tube, in which the retarding potential used was 0.5 volts.   The plot shows the existence of the resonance potential at 4.89 volts, corresponding to λ2537.

TABLE 1.1

CRITICAL POTENTIALS AND TRANSITIONS FOR HELIUM

Spectral Notation	$\lambda(\text{Å})$	Volts	
		Spectroscopic	Electron Impact
$1^1S_0 - 2^3S_1$			19.75
$- 2^1S_0$	600.5	20.55	20.55
$- 2^1P_1$	584.4	21.11	21.2
$- 3^1P_1$	537.1	22.97	22.9
1^1S_0 (Ionization)		24.465	24.47

Table 1.1 gives the values of the critical potentials for helium as measured by Franck and Knipping [1] with the corresponding spectral terms as determined from Lyman's [2] observations.

Table 1.2, taken from the Report on Critical Potentials by Compton and Mohler gives similar data for the alkali group elements.

TABLE 1.2 *

CRITICAL POTENTIALS AND RELATED SERIES TERMS, ALKALI METALS

Element	$\bar{\nu}$ for $1^2S_{1/2}$	V_i		$1^2S_{1/2} - 2^2P_{1/2,3/2}$		V_r	
		Comp.	Obs.	$\bar{\nu}(\text{cm.}^{-1})$	$\lambda(\text{Å})$	Comp.	Obs.
Li	43486	5.368	—	14904	6707.9	1.840	—
Na	41449	5.116	5.13	$\begin{cases}16973\\16956\end{cases}$	5890.0 5895.9	$\left.\begin{matrix}2.095\\2.093\end{matrix}\right\}$	2.12
K	35006	4.321	4.1	$\begin{cases}13043\\12985\end{cases}$	7664.9 7669.0	$\left.\begin{matrix}1.610\\1.603\end{matrix}\right\}$	1.55
Rb	33689	4.159	4.1	$\begin{cases}12817\\12579\end{cases}$	7800.3 7947.6	$\left.\begin{matrix}1.582\\1.553\end{matrix}\right\}$	1.6
Cs	31405	3.877	3.9	$\begin{cases}11732\\11178\end{cases}$	8521.1 8943.5	$\left.\begin{matrix}1.448\\1.380\end{matrix}\right\}$	1.48

* The values of V_i and V_r are computed on the basis of the relation used previously, $V(\text{volts}) = 1.2344 \times 10^{-4}\,\bar{\nu}$.   The values of $\bar{\nu}$ are taken from ref. B. G.

[1] J. Franck and P. Knipping, *Physik. Z.*, **20**, 484 (1919); J. Franck, *Z. Physik*, **11**, 155 (1922).

[2] T. Lyman, *Nature*, **110**, 278 (1922).

In view of the fact that it is possible to measure wave numbers with a very high degree of precision (better than 1 part in 10^6), it is not surprising that efforts have been made to derive accurate values of h/e from measurements of critical potentials. For this purpose, equation (1.13a) can be written in the form

$$\frac{h}{e} = \frac{V_c 10^8}{\bar{\nu}c^2},$$
(1.15)

where V_c is expressed in absolute volts, e in e.s.u., and h in erg sec.

By noting the minimum voltage at which electrons directed into mercury vapor produce ionization of the atoms, E. O. Lawrence[1] determined for the ionization potential the value 10.40 ± 0.02 int. volts.[2] Since the wave number for the limit of the principal series is $84,178.5$ cm.$^{-1}$, we obtain for the ratio h/e the value

$$\frac{h}{e} = \frac{10^8}{c^2} \cdot \frac{10.40}{84,178.5} = 1.375 \times 10^{-17} \text{ erg sec./e.s.u.}$$

L. C. Van Atta[3] measured the excitation potentials of a number of lines in helium, neon and argon. Thus his observations constitute a refinement of those previously made by Franck and Knipping and others. Referring to Table 1.3 the values observed by Van Atta for the excitation of the two helium lines corresponding to the spectroscopic values 21.11 and 22.97 were 21.13 and 23.02 volts respectively. F. G. Dunnington[4] finds that for the five lines investigated the weighted mean value is

$$h/e = (1.3753 \pm 0.0025)10^{-17} \text{ erg sec./e.s.u.}$$

These and other transitions in the spectra of helium, neon and argon have been investigated more recently by R. Whiddington and E. G. Woodroofe[5] by a method[6] involving a precise determination of the energy losses of the electrons on collision with the atoms. Their results are summarized in Table 1.3 taken from their paper.

From six of these lines, "the precision of which," according to Dunnington, "was fairly good and the spectroscopic classification reasonably certain," he

---

[1] *Phys. Rev.*, **28**, 947 (1926). These observations and those of the other investigators discussed in this section have been examined critically in the report by F. G. Dunnington, *Rev. Mod. Phys.*, **11**, 65 (1939), which the reader should consult for more complete details regarding various corrections. ,

[2] For very accurate determinations a correction should be introduced to convert international (int.), to absolute volts (abs. volts). This factor is 1.00041 according to F. G. Dunnington (*Rev. Mod. Phys.*, **11**, 65 (1939) and 1.00034 according to H. T. Wensel (*J. Res. Nat. Bur. Stand.*, **22**, 375 (1939)).

[3] *Phys. Rev.*, **38**, 876 (1931); **39**, 1012 (1932).

[4] *Loc. cit.*

[5] *Phil. Mag.*, **20**, 1109 (1935).

[6] J. E. Roberts and R. Whiddington, *ibid.*, **12**, 962 (1931).

TABLE 1.3

CRITICAL POTENTIALS FOR RARE GASES

Atom	Energy Loss	Transition	Spectroscopic Value *
He	21.11 ± 0.03	$1^1S_0 - 2^1P_1$	21.11
	23.06 ± 0.06	$- 3^1P_1$	22.97
Ne	16.76 ± 0.02	$1^1S_0 - 2^1P_1$	16.76
	18.62 ± 0.05	$- 2^3P_2$	18.62
		$- 3^1P_1$	18.60
A†	11.77 ± 0.03	$1^1S_0 - 1S_2$	11.77
	12.91 ± 0.08	$- 2p_{10}$	12.84
	14.23 ± 0.03	$- 3s_1'$	14.23

* These are calculated on the basis $h/e = 1.374 \times 10^{-17}$

† The notation in this case is that used in the older spectroscopic literature.

concludes a weight mean value,

$$h/e = (1.3737 \pm 0.0018) \times 10^{-17} \text{ erg sec./e.s.u.}$$

On the basis $e = 4.802 \times 10^{-10}$ e.s.u. and $h = 6.6236 \times 10^{-27}$ erg sec., the calculated value is

$$h/e = 1.3793 \times 10^{-17} \text{ erg sec./e.s.u.}$$

which is somewhat higher than that derived from the most accurate determinations of critical potentials available at present.

Data on critical potentials, similar to those already mentioned, have been obtained for a large number of the elements by electron impact methods and in all cases these observations are not only in agreement with spectroscopic data but have also been used frequently to supplement the latter. These investigations will be discussed in a subsequent section in connection with electron configuration in atoms. The main object of the remarks in this section has been to emphasize the extremely important conclusion, which is deduced from the observations on spectral terms and critical potentials, that spectral lines are due to *quantum transitions* between discrete stationary states of atomic systems in accordance with the relation

$$h\nu = E_i - E_f,$$

where E_i and E_f refer to the initial and final states for the emission of a line of frequency ν. Such a conclusion is quite at variance with any classical model for the emission or absorption of radiation. For according to the electromagnetic theory the only conceivable mechanism for the emission or absorption of radiation is an electric doublet oscillating with the *same* frequency ν as the radiation. That the phenomena discussed in this section involve an atomistic

view of the nature of radiant energy is also deduced from other series of investigations, and of these, those dealing with the photoelectric and inverse photoelectric effect are quite remarkable.

(5) **Atomic Number and X-Ray Levels:** An even more striking confirmation of the Bohr theory of energy levels has been furnished by the investigations on characteristic X-ray lines which were initiated by an English investigator, H. G. J. Moseley, shortly before the first World War, which was to cut off what would undoubtedly have been a brilliant scientific career. To understand the significance of his achievement it is necessary to review briefly the nature of the observations upon which have been based our present views on atomic structure.

These views originated from a series of experiments carried out in the Cavendish laboratory during the period 1909–1913. The electron theory had already been developed by J. J. Thomson, H. A. Lorentz and others, while E. Rutherford and F. Soddy formulated their theory of the disintegration of radioactive elements. It was discovered that during the process of disintegration the atoms of these elements emit high velocity charged particles which are known as α- and β-rays respectively. It was shown that α-particles are identical in mass with helium atoms, but differ from the latter in carrying two units of positive electricity. On the other hand, the β-particles are extremely high-speed electrons with velocities ranging from one-tenth to nine-tenths that of light.

Observations by C. T. R. Wilson showed that when α- and β-particles are shot out from a radioactive element through a gas they travel in straight lines for fairly large distances—so large, in fact, that they must, according to all our notions based on the kinetic theory of gases, collide with an extremely large number of molecules on the way. The paths of the α-and β-particles have been photographed by C. T. R. Wilson and other observers by a very ingenious method and these photographs have led to the conclusion that β-particles must pass right through the atoms in their path until they come near enough to an electron in some atom to detach it and thus produce an ion. Similarly the α-particles traverse a large number of atoms before they are deflected, and from the observations on the directions and distribution of the paths of the deflected particles it has been shown that the cause of the deflection must be a strong field of force produced by a positive charge, situated at the center of the atom. The cross-section of this *nuclear* charge is so small that the probability of its being struck by an α-particle is extremely low, even though there are millions of atoms in the path of the particle.

These observations led to the view that the electrons and positive constituent or constituents of the atoms must occupy an extremely small fraction of the total volume of the atom. Practically the whole of the space occupied by an atom must be empty to an α- or β-particle.

More quantitative results regarding the actual dimensions of the positive and negative constituents of the atom were obtained as a result of experiments carried out by Geiger and Marsden in 1909–11. They observed that when

α-rays are allowed to fall on a thin film of gold the majority of the particles pass through with little absorption, but occasionally, approximately in one case out of 20,000, a single particle is thrown back through an angle of more than a right angle.

"Taking into consideration," Rutherford writes,[1] "the great energy of motion of the α-particle, such a result is as surprising as it would be to a gunner if an occasional shot at a light target was deflected back towards the gun. It was found that these large deflections must result from an encounter with a single atom. If the forces causing the deflection were electrical, it was at once evident that the electrical field within the atom must be exceedingly intense. The distribution of positive electricity assumed in the Thomson atom [2] was much too diffuse to produce the intense fields required. To overcome this difficulty the writer inverted the rôle of positive electricity. Instead of being distributed through a sphere comparable in size with a sphere of action of the atom, positive electricity is supposed to be concentrated in a very minute volume or nucleus, and the greater part of the mass of the atom is supposed to be resident in this nucleus. The latter is supposed to be surrounded by a distribution of negative electrons extending over a distance comparable with the diameter of the atom as ordinarily understood. On this point of view the α-particle is the minute nucleus of the helium atom, which has lost its two external electrons. In this type of atom the large deviations of the α-particle take place when it passes through the intense electric field close to the nucleus of the colliding atom. The nearer it passes to the nucleus, the greater the deflection of the particle. Assuming that the forces between the α-particle and the nucleus of the colliding atom are mainly electrical and vary according to an inverse square law, the α-particle describes a hyperbolic orbit around the nucleus, and the relative number of α-particles deflected through different angles can be simply calculated."

Rutherford thus assumes that the scattering is due to a positive charge of magnitude Ze (where e is the unit of charge and Z is the number of these units of positive charge present on the nucleus) situated at the center of the atom; and that this nucleus is surrounded by Z electrons uniformly distributed within a sphere of atomic radius. Furthermore, assuming the validity of the inverse square law, as mentioned already, it is possible to calculate not only the relative distribution of the α-particles for the different angles at which they are deflected, but also the minimum distance, b, corresponding to the sum of the radii of the α-particle and the colliding atom.

Geiger and Marsden showed that the actually observed distribution is in accordance with the conclusion based on the assumption of the inverse square law. Also, from their results, it may be shown readily that the radius of the nucleus of the gold atom cannot exceed 3×10^{-12} cm., which is about one ten-thousandth part of the diameter of the atom. In the case of the scattering of α-particles by hydrogen, where the mass of the nucleus is only one fourth that of the α-particle, we would expect to find, from ordinary dynamical considerations, that some of the hydrogen atoms could be made to recoil four times as far as the penetrating distance (or range) of the α-particle. Marsden showed

[1] The Constitution of Matter and the Evolution of the Elements, Smithsonian Report for 1915, pp. 167–202.

[2] According to the theory developed by J. J. Thomson some years previously, the atom was considered as consisting of a *uniform sphere of positive electrification throughout which* the electrons were distributed uniformly.

that this actually occurs, and it can be calculated that, in this case, the centers of the nuclei must approach to within 10^{-13} cm. of each other. This is a smaller distance than even the diameter of the electron, which, if we assume its whole mass to be electromagnetic in origin, is approximately 1.90×10^{-13} cm. Thus the nucleus, which contains practically the whole mass of the atom, is nevertheless infinitesimally small as compared with the diameter of the atom. From the observations on the disintegration of the radioactive elements during the course of which both α-particles and extremely high speed electrons are ejected, we are driven to the further conclusion that the nucleus itself is an extremely complex structure.

Formerly the view was held that the fundamental units of nuclear structure are the *proton*, that is the nucleus of the hydrogen atom, and the electron. However, in 1932, Cockcroft and Walton demonstrated the disintegration of atomic nuclei by high speed protons, and C. D. Anderson discovered the existence of *positrons*, corpuscles of approximately the same mass as electrons, but having a charge of opposite sign. Then came in 1933, the discovery by J. Chadwick, of a new particle of approximately the same mass as the proton, but possessing no electric charge, which has been designated the *neutron*. As a result of these observations and others which have given a tremendous impulse to the investigation of nuclear phenomena, we now believe that the nucleus is built up of neutrons and protons.*

According to this view of atomic structure each element has a different nuclear charge and therefore a different number of electrons external to this nucleus, since the charge on the nucleus must be equal to the total charge on the electrons. The scattering experiments led to the conclusion that the nuclear charge Z (measured with the electronic charge as unit) is about half the atomic weight for the lighter elements, and rather less than half for the heavier. Earlier observations of C. G. Barkla on the scattering of X-rays were also found to be in accord with this conclusion. In 1913, van den Broek suggested that Z probably represents also the ordinal number which determines the position of the element in the periodic table, while in 1914 Rydberg pointed out that the properties of the elements are determined not by the atomic weight but by the position of the element in the periodic table.

It remained for H. G. J. Moseley[1] to point out a method by which the magnitude of Z could be determined. If a stream of electrons is directed against any solid, X-rays are obtained. This observation constitutes the basis of both the original gas-filled Roentgen-ray tube and the more modern Coolidge tube in which electrons are accelerated from a hot cathode, in a good vacuum, by the application of very high positive voltages on the anode or target. It was discovered very early that the "hardness," or penetrating power, of the rays increases with the anode voltage, and after von Laue, Friedrich and Knipping

---

* For a semi-popular account of these investigations up to 1935, see R. A. Millikan, Electrons (+ and −), Protons, Photons, Neutrons, and Cosmic Rays, Chicago University Press (1935). (Ref., R. A. M.)

[1] *Phil. Mag.*, **26**, 1024 (1913); **27**, 703 (1914).

demonstrated in 1913, by using a calcite crystal as a diffraction grating, that X-rays are of the same nature as ultra-violet and visible radiations but of much shorter wave length, the observation was made that increased hardness of the rays corresponds to decreased wave length.*

An examination of the radiation obtained from an X-ray tube for the distribution of intensity as a function of wave length shows a *continuous spectrum* which increases from very low values at the longer wave lengths, passes through a maximum, and then decreases rapidly with decrease in wave length, to zero at a definite wave length. If the voltage used exceeds a certain value which is characteristic of the anode material, there are also observed one or more peaks superimposed upon the continuous spectrum, which are of considerably greater intensity than the general or "white" radiation.
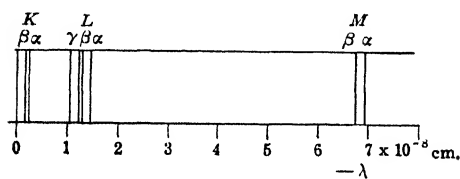

Fig. 1.10.   *K, L* and *M* Series in X-Ray Spectra

For each element it is thus possible to obtain a series of monochromatic X-radiations. These rays as shown in Fig. 1.10, which is a typical spectrum, are classified according to their wave lengths into groups known as *K, L, M,* etc. Moseley carried out an investigation in which he measured the wave lengths of the lines in the *K-* and *L*-series for most of the elements. He found that the spectra of the different elements, beginning with that of aluminum, and ending with that of gold, could be arranged in the same order as in the periodic table, and that under these conditions the wave length of any one characteristic line of the *K-* or *L*-series decreased regularly with increase in the ordinal number of the element in the table. Furthermore, Moseley found that if he assigned to each element a number, *Z*, corresponding to its place in the periodic table (Al = 13, Si = 14, etc., as far as Au = 79), there exists for each type of radiation a simple relation of the form

$$\sqrt{\nu} = a(Z - \sigma),$$

where ν is the frequency, and a and σ are constants.

These measurements have been repeated and extended by M. de Broglie, M. Siegbahn and others.[1] Fig. 1.11 shows the *K*-series for some of the elements between As and Rh as photographed by Siegbahn. The dark line on the extreme left hand corresponds to zero wave length. On closer examination the first line in each spectrum is found to consist of two lines very close together. These are known as the α_1 and α_2 lines of the *K*-series. The darker lines to the right may also be separated into two lines, known as the β_1 and β_2

* These wave lengths range from 10 to 0.01 Å, approximately. It is customary to express wave lengths in this range in terms of the X-unit, where 1 X-unit = 10^{-3} Å = 10^{-11} cm.

[1] M. Siegbahn has reviewed the observations on X-ray spectra and their relation to Moseley's law in *Jahrb. Rad. Elektronik,* **13,** 296 (1916).

lines of the K-series. Now the significance of Moseley's law is this: If we plot the square root of the frequency, or (what amounts to the same thing) the value of $\sqrt{1/\lambda}$ for any one of these lines, as ordinate against the ordinal number Z, we obtain a straight line for each of these characteristic radiations, as shown in Fig. 1.12. The figure actually shows values of $\sqrt{\bar{\nu}/R}$ where R is the Rydberg constant. The reasons for using this value instead of $\sqrt{\bar{\nu}} = \sqrt{1/\lambda}$
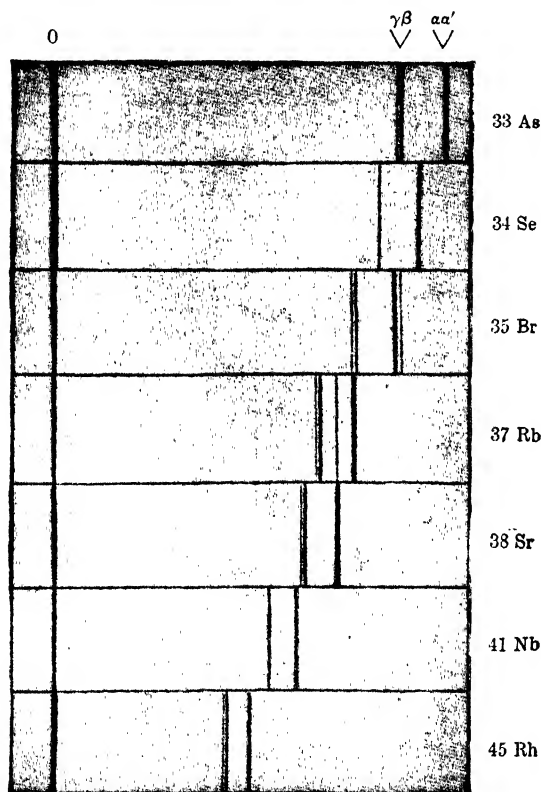

FIG. 1.11. K-Series for Elements As–Rh

are discussed in a subsequent section. The value of Z thus determined is known as the atomic number. That this number also corresponds to the charge on the nucleus has been proved definitely as a result of J. Chadwick's investigations,[1] in which Z was determined directly from careful observations on the scattering of α-particles by different substances.

The fact that such a relation exists which enables us to determine the atomic number, Z, for each element and that this atomic number coincides in all cases

[1] J. Chadwick, *Phil. Mag.*, **40**, 734 (1920).

with the order in which the element must be placed in the periodic table in accordance with its physical and chemical properties, must be regarded as one of the most important discoveries in the history of science.

To the chemist, the periodic arrangement which was first expressed clearly by Mendelejeff has been the most important guiding principle in all speculations upon atomic structure. No matter what property is considered, whether it be atomic volume, compressibility, melting point, valence, or electro-positivity (and electro-negativity), we observe a periodic variation in this function as we pass from the elements of lowest atomic weight to those of highest.[1]
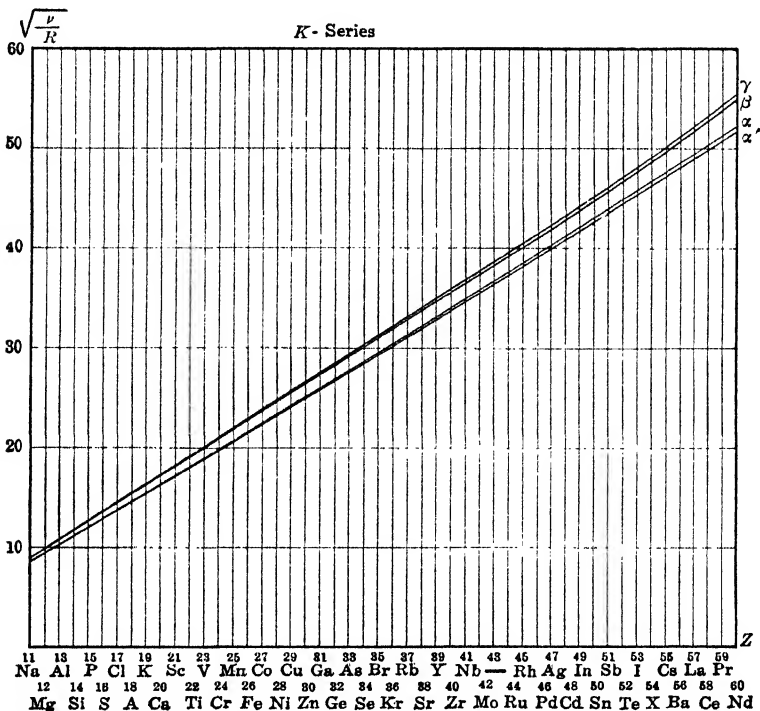

Fig. 1.12. Illustrating Relation Between Frequency and Atomic Number for the *K*-Series in X-Ray Spectra

That, however, the position of any element in the periodic table is not governed primarily by the atomic weight was a belief that gained greater and greater credence as the number of exceptions to the rule increased. Thus the relative positions of argon and potassium, tellurium and iodine, cobalt and nickel as determined by their chemical and physical properties are in the inverse order of their atomic weights. Furthermore, the discovery of isotopes by Aston and others has also served to emphasize the relative unimportance of atomic weight as compared with atomic number. As is well known, it was first shown in the case of radioactive elements and subsequently found to be true also for a number of other elements that we may

[1] See especially the paper by W. D. Harkins and R. E. Hall, *J. Am. Chem. Soc.*, **38**, 169 (1916).

have elements of the same atomic number but different atomic weights. Such elements, since they occupy the same place in the periodic arrangement, are known as isotopes. In all their chemical properties and all physical properties (except those which depend upon mass and radioactive properties), the isotopes corresponding to any given atomic number are identical, yet the atomic masses are different.

These facts lead to the conclusion that the charge on the nucleus, or atomic number, governs all the physical and chemical properties of the atom (except, of course, the radioactive and gravitational properties which depend upon the structure and mass of the nucleus itself).

Furthermore, in order to account for chemical combination and periodic properties, we must assume that the electrons arranged around the nucleus possess different functions according as they belong to the outer or inner set. The outer electrons are active in chemical combination and conduction of electricity through metals. They also must give rise to the ordinary or optical emission spectra which we know are similar for elements of the same group in the periodic arrangement. The number of electrons in this outer set must undergo periodic change in distribution and number as Z increases.

On the other hand, the inner electrons are unaffected by ordinary chemical operations, but high velocity electrons (such as cathode rays) may stimulate them and thus produce the high-frequency spectra observed by Moseley and others. As pointed out by W. Kossel,[1] the fact that for any one type of monochromatic X-radiation (such as the $K\alpha_1$ line) the frequency varies in a regular manner from elements of low atomic number to those of highest atomic number shows that the periodicity observed in the outer electrons does not extend to the innermost.

From the point of view of the Bohr theory the occurrence of characteristic X-ray lines must be interpreted as due to transitions of the inner electrons

FIG. 1.13. Energies of Electrons in the Molybdenum Atom

between energy levels which are normally filled. Fig. 1.13 * shows such an energy level diagram for molybdenum, in which K, L, M, etc. designate the different levels in order of decreasing energy of binding of electrons. If the
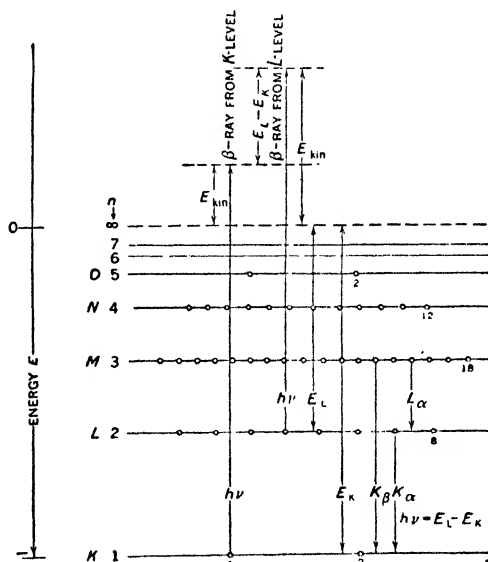
[1] *Ann. Physik*, **49**, 229 (1916).

* From A. H. Compton and S. K. Allison, X-rays in Theory and Experiment, p. 34. MacMillan and Co., London (1935). (Ref. C. A.)

electron incident on the molybdenum anode has acquired the energy E_K (or higher), a secondary electron is ejected from the K-level. The vacant place is now filled by electrons from higher levels, such as the L and M levels, and the transition is accompanied by the emission of the energy difference as a radiation of frequency

$$h\nu_{K\alpha} = E_L - E_K$$

or

$$h\nu_{K\beta} = E_M - E_K,$$

and so forth.

If the energy of the incident electron exceeds E_K, the excess is imparted to the emitted electron in the form of kinetic energy, and by determinations of this quantity it has been possible, as pointed out in a subsequent section, to measure the values of E_K, E_L, etc. very accurately.

As in the case of optical energy levels, the values of this energy for the X-ray levels may be obtained either by absorption measurements or by observations on the critical voltages required for the excitation of the different series.
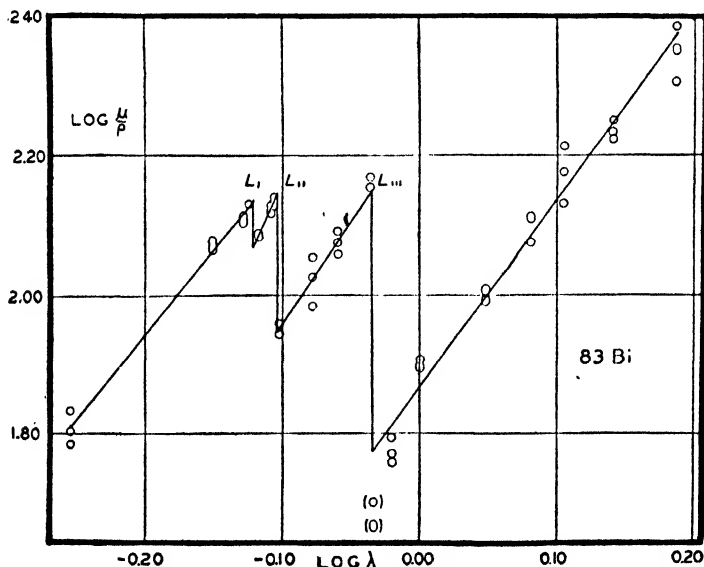

Fig. 1.14.   A Logarithmic Plot of the Mass Absorption Coefficient of Bismuth in the Region of Its L Discontinuities

Figure 1.14 * shows the variation with wave length in the mass absorption coefficient of bismuth, in the region of its L discontinuities. The value of λ at which a jump in absorption coefficient occurs corresponds to an energy of

* Ref. C. A., p. 527.

binding in accordance with a relation of the form

$$h\nu_L = E_L.$$

The presence of these discrete peaks in the absorption spectra of X-rays is indeed additional evidence not only for the existence of energy levels of electrons in atomic systems, but also for the Planck-Einstein view that radiation is emitted or absorbed in units of magnitude $h\nu$.

The other method for determining energy levels is illustrated in Fig. 1.15 * in which the ionization current produced by the X-rays is plotted against the voltage applied to the anode. In this case the latter consisted of rhodium and it will be observed that there was a rapid rise in ionization current at just above 23.2 kilovolts. At this voltage *all* the lines of the K-series appeared
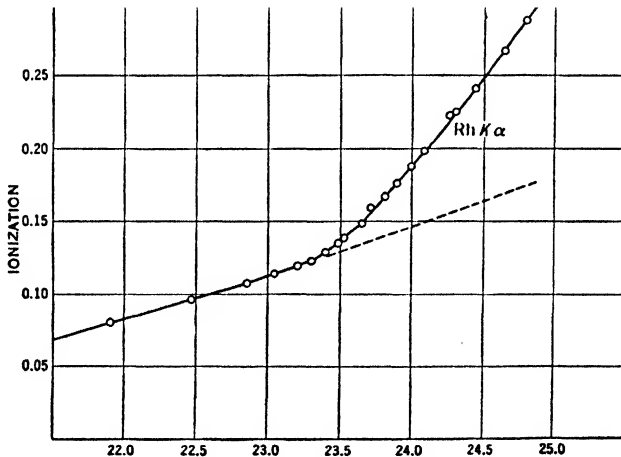

Fig. 1.15. Excitation of the Rh-K_a Line by Electron Bombardment

and further increase in voltage increased the absolute intensities of the lines but left their relative intensities unaltered. Evidently 23.2 kv. corresponds to the energy of binding of the electrons in the K-level, and once an electron is ejected from this level, all the lines appear that correspond to transitions to the K-level from higher levels. This accounts for the fact that the $K\alpha$ line, for which the energy of excitation is 20.1 kv., did not appear until the voltage was raised to the higher value, 23.2 kv.

As a result of a large number of investigations of the type discussed there are now available very accurate values on the X-ray energy levels for most of the elements. The application of these data to the elucidation of electron configuration forms an extremely interesting topic which will be discussed in a subsequent section.

* D. L. Webster, *Phys. Rev.*, **7**, 559 (1916); Ref. C. A., p. 587.

2. Photoelectric Effect *

(1) Einstein's Law: When the negatively charged surface of a metal, such as zinc or sodium, is illuminated by light of very short wave length, electrons are emitted. The method used in experiments on this effect is quite simple in principle. An evacuated bulb containing the surface under investigation as one electrode and a grid or plate as the other electrode, is connected in series with a battery and galvanometer. As the potential on the photo-emitting surface is made more and more negative with respect to the other electrode the current increases and finally reaches an approximately constant value which varies directly with the intensity of the illumination. That is, the saturation electron emission is proportional to the intensity of the incident light.

The spectral sensitivity of the surface depends upon the nature of the metal used. Thus, while zinc or cadmium responds only to radiation in the far ultra-violet, sodium is sensitive to the nearer ultra-violet and from a surface of cesium prepared by suitable treatment, electrons are emitted by radiation in the near infra-red ($\lambda > 7000\text{Å}$).

This is in agreement with the observation that for each type of surface there exists a minimum frequency of radiation (ν_0) for the emission of electrons. It has also been found that this *threshold* frequency corresponds to the so-called 'work function' for thermionic emission in accordance with the relation

$$h\nu_0 = \phi_0 e = k b_0, \tag{2.1}$$

where ϕ_0 = the work function (expressed in electron volts),

k = Boltzmann's constant; and b_0 = Richardson's constant in the thermionic emission relation,[1]

$I = A T^2 e^{-b_0/T}$.

From the point of view of the quantum theory this relation is extremely significant. But even more important are the observations which have been made on the relation between frequency of incident radiation and kinetic energy of emitted electrons. The latter may be determined, in accordance with the relation,

$$E = mv^2/2 = Ve,$$

by noting the magnitude of the *retarding* potential, V, required to reduce the electron current to zero. Now, according to any wave theory of light the energy of the emitted electrons should vary directly as the square of the amplitude of the electric vector, that is, directly as the intensity of the light,

---

* For further references on this topic the reader should consult the following:

A. Ll. Hughes and L. A. DuBridge, Photoelectric Phenomena, McGraw-Hill (1932)—an extremely comprehensive treatise. (Ref. H. D.)

L. A. DuBridge, New Theories of the Photoelectric Effect, Hermann, Paris (1935).

L. R. Koller, The Physics of Electron Tubes, Second Edition, McGraw-Hill (1937) contains a discussion of the more technical aspects. See also refs. F. K. R. and H. L.

[1] See, for instance, ref. H. L., Chap. 6, or L. R. Koller, *op. cit.*

and should be independent of the frequency. Actual observations showed, however, that while the *rate of emission* of electrons is proportional to the intensity of the incident radiation, the kinetic energy of the electrons varies linearly with the frequency in accordance with the relation

$$\tfrac{1}{2}\, mv^2 \;=\; Ve \;=\; h(\nu - \nu_0), \tag{2.2}$$

where ν_0, as mentioned already, is the photoelectric threshold frequency and V is the retarding potential on the receiving electrode.

The simplest interpretation of this equation is that the incident radiation behaves as if constituted of energy "bundles," or *photons*, each of magnitude $h\nu$. If this magnitude exceeds the value kb_0 required for the passage of an electron through the potential barrier at the surface then it is possible for an electron to be emitted and the excess energy $(h\nu - kb_0)$ is imparted to the electron as kinetic energy.

This equation was first suggested by A. Einstein in 1905 as a consequence of Planck's theory. However, many of the earlier attempts to test the validity of the equation did not succeed, and it was only as the result of a series of investigations carried out by R. A. Millikan and his students, during 1915–1917, that actual confirmation of Einstein's relation was obtained.[1]

Plotting the values of the maximum retarding potential against the frequency, a straight line is obtained, the slope of which, according to Einstein's equation gives the value of h/e.

The values of this ratio which Millikan obtained for sodium and for lithium were 1.374 and 1.379 $\times 10^{-17}$, respectively, which, on the basis $e = 4.803 \times 10^{-10}$ e.s.u., lead to the values $h = 6.605$ and 6.628×10^{-27} erg sec., respectively.[2] Similar investigations were carried out, in Millikan's laboratory, on magnesium and aluminum by A. E. Henning and W. H. Kadesch[3] and on cadmium and copper by A. E. Sabine,[4] all demonstrating the validity of Einstein's relation.

More recently P. Lukirsky and S. Prileẑaev[5] have carried out similar measurements with surfaces of Al, Zn, Sn, Ni, Ag, Cd, Pb, Cu and Pt, using a number of lines in the mercury spectrum ranging from $\lambda2302$ to $\lambda3130$. Fig. 2.1, taken from their paper, shows a plot of current (I) versus retarding voltage (V) for Al at three different wave lengths. (Curve 1 with $\lambda2302$, 2 with $\lambda2537$ and 3 with $\lambda3130$.) These plots demonstrate one of the inherent difficulties in this method of determining h/e, due to the asymptotic form of the curve for very small values of I. It was found that in this region the curves could be represented by an empirical equation of the form $\sqrt{I} = A(V_m - V)$ where V_m is the maximum retarding potential. Fig. 2.2 shows graphs, obtained in this manner, for V_m versus ν for a series of metals.

[1] For a semi-popular account of this work see ref. R. A. M.

[2] Millikan's values for h/e should also be corrected for the difference in the value for the velocity of light used by him and that accepted at present.

[3] *Phys. Rev.*, **8**, 209, 221 (1916).

[4] *Ibid.*, **9**, 260 (1917).

[5] *Z. Physik*, **49**, 236 (1928).

From a consideration of these observations, Birge has deduced a value $h = (6.543 \pm 0.01) \times 10^{-27}$ erg sec. based on the value $e = 4.774 \times 10^{-10}$ e.s.u.

The only other careful measurements in this field are those obtained by A. R. Olpin [1] with sodium, from which, according to H. T. Wensel [2] the most likely value is $h/e = 1.3748 \times 10^{-17}$.
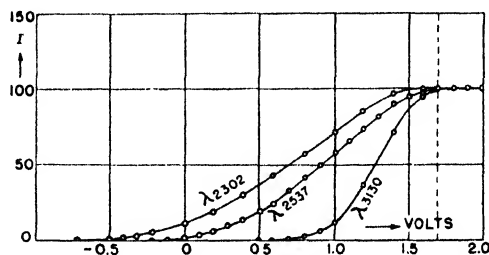

FIG. 2.1.   Plot of Photoelectric Current versus Retarding Voltage for Al, at Three Different Wave Lengths

On the whole it would seem that as a method for the accurate determination of h/e (and hence of h) the measurements involving the photoelectric effect are not to be regarded as highly as other methods which will be described in the following sections.   One difficulty, which has been mentioned already, is that theoretically Einstein's relation is valid only for $T = 0$.   Both the maximum
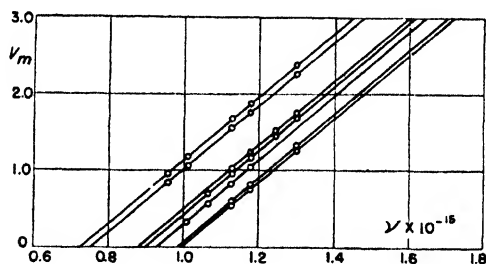

FIG. 2.2.   Plots of V_m versus ν for Series of Metals.   The slope $\Delta V/\Delta\nu = h/e$.   From left to right the plots refer to Al, Zn, Sn, Ni, Gd, Cu, Pt

retarding potential (V_m) for a given frequency and the work function (ϕ_0) probably vary slightly with temperature.   As DuBridge has pointed out [3] it is possible, in some cases, to obtain as much as 1 per cent difference in the values of h/e, depending upon whether an empirical extrapolation method is

---

[1] *Phys. Rev.*, **36**, 251 (1930).

[2] *J. Res. Natl. Bur. Stand.*, **22**, 375 (1939).

[3] New Theories of the Photoelectric Effect, Hermann, Paris (1935), pp. 51–53.   See also in this connection the remarks by M. M. Mann and L. A. DuBridge, *Phys. Rev.*, **51**, 120 (1937); W. V. Houston, *ibid.*, **52**, 1047 (1937); C. F. J. Overhage, *ibid.*, **52**, 1040 (1937); J. W. M. DuMond, *ibid.*, **56**, 153 (1939).

used for determining V_m or a value is calculated on the basis of a theory of the variation with temperature, of the photo-current at a given retarding potential.

(2) **Photoelectric Effects of X-Rays:** Since X-rays and γ-rays are of the same nature as ultra-violet radiations but of very much shorter wave length, it would be expected that they would also produce photoelectric effects similar to those described in the previous section, and a large number of investigations have confirmed this expectation. The results of these investigations have been summarized by Hughes and DuBridge as follows: *

1. "The Einstein equation has been precisely confirmed for photoelectrons ejected by all frequencies up to those of the hardest γ-rays . . . thus establishing it as one of the most far-reaching and fundamental relations in all physics.

2. "It has been discovered that the Einstein equation holds also for the inverse photoelectric process (the production of radiation, e.g., X-rays, by electrons), and this discovery has yielded a highly precise method for determining the value of Planck's constant.

3. "By measuring the velocity of photoelectrons ejected from atoms by X-rays and γ-rays it has been found possible to obtain directly accurate experimental values for the atomic energy levels, and also for the wave lengths of the incident radiation. In some cases these cannot be accurately determined by any other method.

4. "Experiments have yielded information as to the nature of the photoelectric process itself which could never have been obtained through experiments with ultra-violet light."

Some of the first observations which threw doubt on the universal validity of the wave theory of light were those concerned with the ionization of atoms by X-rays. It was observed that when X-rays pass through a gas they ionize only about one in a thousand billion of the atoms or molecules which are actually in the path of the rays. Apparently the rays do not lose any energy whatever for quite a distance, while they pass over billions of molecules, and then, for some unexplained reason, one molecule absorbs the energy of a whole train of X-ray waves and an electron is ejected. Furthermore, the *maximum energy acquired by the ejected electron is related to the frequency, ν, by the Einstein relation* (see equation (2.2)),

$$E = h\nu. \tag{2.3}$$

Similarly when X-rays strike the surface of a metal the maximum energy of the electrons emitted is given by this equation which is the same as the relation for the optical photoelectron emission equation except for the omission of the term involving the work function. Since $h\nu$ in the case of X-rays corresponds to thousands of electron volts, the energy required to pass through the surface potential barrier becomes negligible in comparison.

In attempting to test the validity of equation (2.3) for metals it has been necessary to devise methods for determining the energy distribution of the emitted electrons. Since the method involving the measurement of retarding potentials has practical limitations for electrons having very high velocities, a magnetic deflection method has been used. In this method,[1] originally

---

* Ref. H. D., Chapter XI.

[1] It was first applied to this problem by H. R. Robinson and W. F. Rawlinson, *Phil. Mag.*, **28**, 277 (1914) and has been developed by the first named investigator and his associates into a very accurate method for the determination of X-ray levels, e/m, and h/e.

developed for the measurement of e/m, a very narrow beam of the electrons is sent through a magnetic field of strength H, the direction of which is at right angles to that of the electrons at the origin. The latter are deflected into a circle of radius r, which depends upon the velocity of the electrons and the field H. By means of a photographic plate or other detector the value of r (and consequently that of the energy) may be determined with a high degree of accuracy. The theory underlying the method is as follows:

The force due to the field H acting on an electron having the velocity v, is Hev. This must be equal to the centripetal force mv^2/r. Hence,

$$v = \left(\frac{e}{m} \right) Hr. \tag{2.4}$$

In the case of electrons with velocities such that $\beta = v/c$ (where c = velocity of light) is not negligible compared to unity, the mass is a function of v in accordance with the relativity equation,

$$m = \frac{m_0}{\sqrt{1 - \beta^2}}, \tag{2.5}$$

where m_0 is the "rest mass" of the electron.

Hence, equation (2.4) becomes

$$Hr = \frac{m_0}{e} \cdot \frac{\beta c}{\sqrt{1 - \beta^2}} \tag{2.6}$$

and for the kinetic energy of the electron we obtain the relation,

$$E_T = m_0 c^2 \left[\frac{1}{\sqrt{1 - \beta^2}} - 1 \right] \tag{2.7a}$$

$$= m_0 c^2 \left[\sqrt{1 + H^2 r^2 \left(\frac{e}{m_0 c} \right)^2} - 1 \right]. \tag{2.7b}$$

Using this method M. de Broglie [1] was the first of a number of investigators to obtain remarkable confirmation of the validity of equation (2.3) for electron ejection by monochromatic X-rays. When these are made to fall on very thin metal foils, the emitted electrons exhibit a magnetic spectrum which consists of very sharp lines, and consequently the corresponding values of E may be calculated very accurately.

Let us consider now the interpretation of these observations. The energy of the incident radiation of frequency ν is used, first in removing the electron from an inner level of the atom, for which the energy of binding is E_B, and secondly, in imparting to the emitted electron a kinetic energy E_T, the maximum value of which is determined in accordance with equation (2.7b) by the

[1] *J. phys. rad.*, **2**, 265 (1921).

corresponding value for r on the photographic plate; that is,

$$h\nu = E_T + E_B. \tag{2.8}$$

Now E_B should be identical with some one of the terms E_K, E_L, etc. which, as stated in a previous paragraph, correspond to the energies of binding of an electron in the K-, L-, etc. levels. Since these are discrete energy values it follows that for a given value of ν, the values of E_T should also form a discrete series of values, and should show up as a discrete series of values of r in the magnetic spectrum. As Hughes and DuBridge point out, "The fact that such a distribution (of energies) is actually observed constitutes possibly the strongest direct evidence for the physical reality of discrete energy levels."

For convenience in comparing the values of E_B calculated by means of the last equation with spectroscopically measured energy levels it is customary to express the equation in the form

$$\frac{\tilde{\nu}}{R_\infty} = \frac{\tilde{\nu}_P}{R_\infty} + \frac{\tilde{\nu}_B}{R_\infty}, \tag{2.9}$$

where R_∞ is the Rydberg constant for infinite mass, $\tilde{\nu}$ is the wave number for the incident radiation, $\tilde{\nu}_B$ the wave number of the energy level from which the electron is ejected and $\tilde{\nu}_P$ is the wave number equivalent of the energy of the emitted photoelectron. The values thus derived may be converted into electron volts by multiplying by the factor $10^{-8}c^2hR_\infty/e = 13.60$.

As an illustration of the validity of this equation, Table 2.1 shows a set of data obtained by H. R. Robinson and his associates [1] on the maximum energies for photoelectrons ejected from gold by the characteristic $K\beta_1$ radiation from molybdenum, for which $\tilde{\nu}/R_\infty = 1444.7$. The first column gives the observed values of Hr and the second, the values for $\beta = v/c$, calculated by means of equation (2.6) which for Hr in terms of gauss cm. takes the form,

$$\frac{\beta}{\sqrt{1 - \beta^2}} = 5.868 \times 10^{-4}\, r\mathrm{H}.$$

From equation (2.7a) the energy in terms of the Rydberg constant is then deduced by means of the relation

$$\frac{\nu_P}{R_\infty} = \frac{m_0c^2}{hcR_\infty}\left(\frac{1}{\sqrt{1 - \beta^2}} - 1 \right)$$

$$= 3.756 \times 10^4\left(\frac{1}{\sqrt{1 - \beta^2}} - 1 \right).$$

---

[1] This work has been carried on over a period of 20 years and is published in the *Proc. Roy. Soc.*, [A], *Phil. Mag.* and *Proc. Phys. Soc.* A summary of this work is given in *Phil. Mag.*, **22**, 1129 (1936). See also, Ref. H. D., Table 11-1, p. 397.

* The constants used in calculating the data shown in Table 2.1 are not quite the same as those given in this and the previous equation because of the difference in accepted values of the fundamental constants. In this table R is used instead of R_∞.

The fourth and fifth columns give the values of $\bar{\nu}_B/R$ calculated and observed, respectively, the latter being obtained from the spectroscopic values for the energy levels indicated in the last column.

TABLE 2.1

ENERGIES OF PHOTOELECTRONS EJECTED FROM GOLD BY Mo $K\beta_1$ RADIATION
($\bar{\nu}/R = 1444.7$)

Hr	β	$\bar{\nu}_P/R$	$\bar{\nu}_B/R$ calc.	$\bar{\nu}_B/R$ obs.	Origin
244.0	0.1418	386.8	1059.2	1060.2	L_I
257.9	.1496	431.8	1012.5	1014.2	L_{II}
296.0	.1712	567.9	878.5	878.5	L_{III}
431.5	.2455	1196.0	252.9	252.9	M_I
440.4	.2502	1246.0	201.8	202.8	M_{III}
447.6	.2540	1286.4	163.0	163.0	M_V
468.5	.2651	1407.2	41.8	41.8	N_{I-III}

According to H. R. Robinson, J. P. Andrews and E. J. Irons [1] the difference between the "photoelectric" and "spectroscopic" values of $\bar{\nu}$ obtained under conditions in which an attempt was made to secure a high degree of accuracy, is about 0.5 per cent on the average, which is probably due to our present state of uncertainty regarding the exact values of some of the fundamental constants. An examination by F. G. Dunnington [2] of the large amount of data published by Robinson and his associates, leads him to deduce from these data the result,

$$(e/m_0)(e/h) = (3.8220 \pm 0.0029)10^{34} \text{ e.s.u.}$$

More recently R. L. Mayo and H. R. Robinson [3] and C. J. Birkett Clews and H. R. Robinson [4] have measured the energies of electrons expelled from metals by silver $K\alpha_1$ radiations and gold L-radiations. Assuming Birge's values for e/m and e, they derived the result $h = 6.629 \times 10^{-27}$, which is in good agreement with the value deduced by Birge by use of the Rydberg constant.

Careful measurements on the energies of photoelectrons ejected by X-rays have also been made by G. G. Kretschmar [5] and from these data Dunnington derives the value

$$(e/m_0)(e/h) = 3.8067 \times 10^{34} \text{ e.s.u.}$$

If we accept the value $e/m_0 = 5.2734 \times 10^{17}$ abs. e.s.u. gm.$^{-1}$, the values derived for h/e are as follows:

> Robinson's data: 1.380×10^{-17} erg sec. e.s.u.$^{-1}$
> Kretschmar's data: 1.385×10^{-17}.

[1] *Proc. Roy. Soc.*, [A], **143**, 48 (1934).

[2] *Loc. cit.*

[3] *Proc. Roy. Soc.*, [A], **173**, 192 (1939).

[4] *Ibid.*, **176**, 28 (1940).

[5] *Phys. Rev.*, **43**, 417 (1933).

(3) **Auger Effect** [1] **and Photoelectric Emission by Gamma Rays:** Actually, the electrons ejected from a metal by incident X-rays fall into two groups. The first group, known as "X-ray electrons," has been discussed in the previous section. In this case the energy of the emitted electrons is obtained from that of the incident photon. However, with the development of more sensitive X-ray spectrometers, lines were observed, which did not seem to fit into the conventional energy level diagram. These lines are rather faint, and are usually observed associated with the more intense "diagram" lines. Hence they are designated as "satellites." The occurrence of these lines was interpreted by D. Coster and R. de L. Kronig [2] as due to an internal photoelectric effect of the same nature as that previously observed by P. Auger. [3]

In a Wilson cloud chamber ionized by X-rays, Auger observed short, fat tracks, the lengths of which were independent of the frequency of the X-rays; but were dependent on the kind of atoms in the chamber. Auger explained these tracks as follows: "In the ordinary process by which an atom radiates, an electron falls from, say, the M_V subshell into a vacancy, in, say, the L_{III} shell, and a quantum, in this case $L\alpha_1$, is emitted.

"But suppose that initially an L_1 electron is missing. Then let an L_{III} electron, say, drop into the vacant place, thereby freeing energy $(E_{L_I} - E_{L_{III}})$, and let this quantum of energy on its way out be photoelectrically absorbed in, for example, the M_{IV} subshell causing the emission of an M_{IV} electron. The atom will be left doubly ionized $(L_{III} + M_{IV})$; and will be in the initial condition required to produce an $L\alpha$ satellite, if either an M_{IV} or M_V electron drops into the vacant L_{III} shell. However, an M_{IV} or M_V electron will be expelled *only if the energy released* $(E_{L_I} - E_{L_{III}})$ *is sufficient to expel that electron.*" [4]

It is the electrons released from a metal by such a process that constitute the second group or "Auger" electrons. Since the atom from which these electrons are expelled is left multiply-ionized, their energy cannot be described by a simple Einstein relation. However, it is possible, as shown by R. L. Mayo and H. R. Robinson [5] to measure this energy by the magnetic method described in the previous section and thus determine the energy distribution.

The observations on the emission of electrons by γ-rays are in accord with those to be expected in view of the fact that the magnitudes of the energy quanta are much larger than in the case of X-rays. Consequently these radiations are able to eject electrons from the K-levels of the elements of highest atomic number. Thus, in the case of uranium $(Z = 92)$ the binding energy for electrons in the deepest of the K-levels is 115,800 volts. When γ-rays having a wave length of 34.9 X-units $(34.9 \times 10^{-11}$ cm.) and corresponding to an energy quantum of 353,000 electron volts, are absorbed by uranium, high

[1] For a comprehensive review of this topic see F. K. Richtmeyer, *Rev. Mod. Phys.*, 9, 391 (1937).

[2] *Physica*, 2, 13 (1935).

[3] *Compt. rend.*, 180, 65 (1925); 182, 773 (1926).

[4] F. K. Richtmeyer, *loc. cit.*, p. 397.

[5] *Proc. Roy. Soc.*, [A], 173, 192 (1939).

speed photoelectrons or β-particles are ejected with a maximum kinetic energy of 237,200 electron volts. Thus, while most of the β-rays emitted during the disintegration of radioactive atoms have their origin in the nucleus, some of these high-speed electrons are due to a photoelectric effect on the K-electrons external to the nucleus, as is evidenced by the observation that the latter show up in the velocity spectrum as *lines* on a continuous background. From magnetic deflection determinations of the energies of the photoelectrons ejected by γ-rays and spectroscopic measurements of the limits of the absorption spectrum for K-radiations it has been found possible, by application of Einstein's equation, to determine the wave lengths of the incident γ-rays.

3. INVERSE PHOTOELECTRIC EFFECT

(1) **Application of Effect to Determination of h:** In the previous section the phenomena discussed involved the emission of electrons by the action of incident radiation. However, in an X-ray tube we observe the inverse phenomenon, that is the transfer of energy from electrons accelerated by the anode voltage to radiation emitted by the target. As mentioned already, this radiation exhibits a continuous spectrum at lower voltages, upon which are superimposed, at higher voltages, intense lines characteristic of the anode material.

What is of special interest in the present connection is the observation that there exists, in the case of the continuous spectrum, a maximum frequency (ν_m) which varies with the anode voltage in accordance with the Einstein relation

$$Ve = h\nu_m. \tag{3.1}$$

In terms of absolute volts and minimum wave length (which is the quantity measured by the crystal spectrometer), this equation assumes the form

$$\frac{V\lambda_m 10^8}{c^2} = \frac{h}{e}, \tag{3.2}$$

where λ_m, h, e, and c are expressed in c.g.s. units.

Here again it is evident, as K. K. Darrow [1] has stated, "Excitation of radiation by electrons stopped in their flight by collision with a metal occurs as if the energy of radiation were concentrated in units of amount $h\nu$, and one such unit were created out of the total energy which each electron surrenders when it is stopped."

Figure 3.1 [2] shows the spectra obtained at five different voltages (below that required to produce the characteristic lines) with a Coolidge tube containing a tungsten anode. It will be observed that the minimum wave length decreases with increase in voltage, and the observations are found to be in very satisfactory agreement with Einstein's relation. Plotting ν_m against V for a range

[1] *Bell Tech. J.*, **4**, No. 2, April (1925).

[2] A. W. Hull, *Am. J. Roentgenology* (Dec. 1915).

of voltages up to 110,000 Hull deduced for the slope of the resulting straight line the value $h/e = 1.381 \times 10^{-17}$ erg sec e.s.u.$^{-1}$.

As a method for the accurate determination of Planck's constant the inverse photoelectric effect has seemed specially attractive. Since λ_m is deduced by means of the Bragg relation

$$n\lambda = 2d \sin \theta,$$

where n is an integer, d is the grating space of the crystal and θ the glancing angle at which the given radiation shows interference, the precision determination of h by means of equation (3.2) involves accurate determinations not only of

FIG. 3.1. Variation in Intensity with Wave Length of X-Rays Emitted at Different Anode Voltages.

V and θ but also of e. For the value of d depends upon that of N, the Avogadro constant, which in turn is given by the relation $N = \mathrm{F}c/e$, where F is the Faraday constant ($= 9648.0$ abs. e.m.u. gm.-equiv.$^{-1}$). Consequently the equation for the determination of h by this method may be written in the form

$$h = Ke^{4/3}V \sin \theta, \qquad (3.3)$$

where K is a function of measured constants (including the density of the crystal used and the constants F and c).

Table 3.1 gives a summary of the values of h/e obtained by a number of investigators. In the case of all but the last three, the values of h/e have been deduced from the published values of h, assuming $e = 4.770 \times 10^{-10}$ e.s.u. The value of $h/e^{3/4}$ actually obtained by Ross and Kirkpatrick was 1.7563×10^{-14} c.g.s. units, while DuMond and Bollman deduced the value 1.7572×10^{-14}. Schaitzberger derived the value $h/e = 1.3728 \times 10^{-17}$ c.g.s. units on the basis $e = 4.774 \times 10^{-10}$ e.s.u. The last three values given in the table are those recalculated by F. G. Dunnington from the original data, on the basis $h = 6.610 \times 10^{-27}$ erg sec. He has also deduced from these results a weighted average value $h/e = 1.3763 \times 10^{-17}$ c.g.s. units, which, combined with $h = 6.61 \times 10^{-27}$ c.g.s. units, yields the result $e = 4.8026 \times 10^{-10}$ e.s.u. As shown in the table of constants the value for h/e recommended by R. T. Birge, on the basis $e = 4.8022 \times 10^{-10}$ e.s.u., and $h = 6.6236 \times 10^{-27}$ erg sec., is $h/e = 1.3793 \times 10^{-17}$ erg sec. e.s.u.$^{-1}$.

It should be pointed out in this connection that the value of d, the grating space, is related to the Avogadro constant N, by the relation
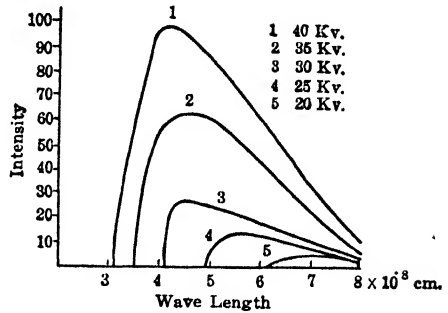
$$N = \frac{M}{2d^3\phi\rho}, \qquad (3.4)$$

where M = molecular mass

ρ = density of crystal lattice

ϕ = factor for determining the volume per molecule, which is calculated from the lattice type.

TABLE 3.1

Observers	Year	$h/e \times 10^{17}$ (erg sec. e.s.u.$^{-1}$)
W. Duane and F. L. Hunt [1]	1915	1.365
A. W. Hull [2]	1915	1.381
D. L. Webster [3]	1916	1.369
F. C. Blake and W. Duane [4]	1917	1.374
E. Wagner [5]	1920	1.370
W. Duane, H. N. Palmer [6] and C. Yeh	1921	1.375
H. Feder [7]	1929	1.373
P. Kirkpatrick and P. A. Ross [8]	1934	1.3754
G. Schaitzberger [9]	1935	1.3773
J. W. DuMond and V. L. Bollman [10]	1937	1.3765

In the work on X-ray wave lengths, until about 1929, the value of N was derived from that of e, by the relation

$$N = Fc/e. \tag{3.5}$$

Wave lengths thus determined are expressed in terms of the Siegbahn unit (X-unit = 10^{-11} cm.). However, with the development in the laboratory of A. H. Compton of a direct method for the measurement of X-ray wave lengths by means of a reflection grating * it was found that the actually measured values are greater than those derived by Siegbahn on the basis of Millikan's value for e. The ratio of the grating to the Siegbahn system of wave lengths, (designated by k_λ) as deduced by Birge, is 1.002034 ± 0.00006.

On the basis of equations (3.4) and (3.5) this result indicates that the value of N as determined from the grating space should be approximately 0.6 per cent less than that deduced from Millikan's value of e. Consequently it was concluded that the latter must be too low by about this amount, as is evident from

[1] *Phys. Rev.*, **6**, 166 (1915).

[2] *Ibid.*, **7**, 156 (1916).

[3] *Ibid.*, **7**, 559 (1916).

[4] *Ibid.*, **10**, 624 (1917).

[5] *Physik. Z.*, **21**, 621 (1920). Table gives the value as re-calculated by R. T. Birge, *Phys. Rev.* (Supplement) **1**, 1 (1929).

[6] *Proc. Nat. Acad. Sci.*, **7**, 237 (1921); *J. Opt. Soc. Am.*, **5**, 213 (1921). Table gives value revised by Birge, *loc. cit.*

[7] *Ann. Physik*, **1**, 497 (1929).

[8] *Phys. Rev.*, **45**, 454 (1934).

[9] *Ann. Physik*, **24**, 84 (1935).

[10] *Phys. Rev.*, **51**, 400 (1937).

* The initial work is described in ref. C. A., and more recent work by F. Kirchner, *Ergebn. exakt. Naturwiss.*, **18**, 26 (1939), who gives copious references to the original sources. See also F. G. Dunnington, *loc. cit.*

a comparison of the earlier value, $e = 4.770 \times 10^{-10}$ with that adopted by Birge.*

(2) **Photons versus Waves:** These observations on the photoelectric and inverse photoelectric effects are remarkable when considered in the light of the wave theory of propagation of energy. As A. H. Compton [1] has pointed out,

"The significance of this work will perhaps be more obvious if we imagine the following experiment: Let two X-ray tubes, A and B, be placed side by side. Tube A is operated at a constant potential of say 100,000 volts. A cathode electron with a kinetic energy Ve strikes the target of tube A and gives rise to an X-ray of frequency $\nu = Ve/h$. This ray strikes the target of tube B and there ejects a photoelectron whose kinetic energy is $Ve - E_B$ (where E_B is the binding energy of the electron in the atom). This means that all of the energy of the cathode electron in tube A has been transmitted to the photoelectron ejected from the target of tube B. How is it possible for such a complete transfer of energy to be effected? . . .

"The impossibility that an electromagnetic wave whose energy spreads in all directions should effect such a sudden and complete transfer of energy is obvious. It is equally clear that Einstein's photon conception affords a simple and adequate method of making the transfer."

Sir William Bragg's remarks on this topic state the contradictions involved in these observations in a very striking manner. [2]

"In order to realize," he writes, "the full significance of these extraordinary results, let us picture the double process as it occurs whenever we use an X-ray bulb. By the imposition of great electrical forces we hurl electrons in a stream across the bulb. One of these electrons, let us say, starts a wave where it falls. This action is quite unaffected by the presence of similar actions in the neighborhood, so that we can fix our minds upon this one electron, and the wave which it alone causes to arise. The wave spreads away, it passes through the walls of the bulb, through the air outside, and somewhere or other in its path in one of the many atoms it passes over, an electron springs into existence, having the same speed as the original electron in the X-ray bulb. The equality of the two speeds is not necessary to the significance of this extraordinary effect; it would have been just as wonderful if one speed had only been one half or one quarter or any reasonable fraction of the other. The equality is more an indication to us of how to look for an explanation than an additional difficulty to be overcome.

"Let me take an analogy. I drop a log of wood into the sea from a height, let us say, of 100 feet. A wave radiates away from where it falls. Here is the corpuscular radiation producing a wave. The wave spreads, its energy is more and more widely distributed, the ripples get less and less in height. At a short distance, a few hundred yards perhaps, the effect will apparently have disappeared. If the water were perfectly free from viscosity and there were no other causes to fritter away the energy of the waves, they would travel, let us say, 1000 miles. By which time the height of the ripples would be, as we can readily imagine, extremely small. Then, at some point on its circumference, the ripple encounters a wooden ship. It may have encountered thousands of ships before that and nothing has happened, but in this one particular case the unexpected happens. One of the ship's timbers suddenly flies up in the air to exactly 100 feet, that is to say, if it got clear away from the ship without having to crash through parts of the rigging or something else of the structure. The problem is, where did the energy come from that shot this plank into the air, and why was its velocity so exactly related to that of the plank which was dropped into the water 1000 miles away? It is this problem that leaves us guessing."

* Certain questions which arose regarding the accuracy of a determination of e by the reflection grating method seem to have been settled by the most recent work. See, for instance, the report by P. H. Miller and J. W. M. DuMond, *Phys. Rev.*, **57**, 198 (1940). The reader will also find a further discussion of this topic in Section 7(6), p. 212.

[1] *Phys. Rev.* (Supplement), **1**, 74 (1929).
[2] *Scientific Monthly*, **14**, 153 (1922).

According to Rayleigh, an electron over which a radiation of wave length, λ, is passing can collect the energy from an area round about it of magnitude λ^2. But, as Bragg points out, "It is not difficult to show that when an X-ray bulb is started and its rays radiate out, the actual amount of energy which can be picked up by an atom a few feet away would not be sufficient for the ejected electron, though the tube were running for months; whereas we find the result to be *instantaneous. . . . The effects are as if the energy were conveyed from place to place in entities, such as Newton's old corpuscular theory of light provides.*"

The wave-theory thus meets with two difficulties in attempting to account for the ejection of electrons by X-rays and ordinary radiation. First, a wave-motion is defined by frequency and amplitude of vibration, while the electron emission is defined by the number and speed of the electrons. The relation between the two is very simple. The number of electrons is proportional to the square of the amplitude of vibration, while the energy of ejection is proportional to the frequency. That the speed of the electron is independent of the intensity is an extraordinary result from the point of view of the wave-theory. The second difficulty encountered by the latter occurs when we attempt to account for the observation that the radiation can apparently pass over so many atoms and then cause ejection of an electron from some one atom at the very instant that the radiation strikes it. *There is no time lag whatever;* there is no opportunity for the atom to store up the energy for subsequent conversion into kinetic energy of the electron.

R. A. Millikan [1] has stated the difficulty of explaining photoelectric emission on the basis of a wave-theory in the following remarks:

"When we attempt to compute on the basis of a spreading wave-theory how much energy a corpuscle can receive from a given source of light, we find it difficult to find anything more than a very minute fraction of the amount which the corpuscle actually acquires.

"Thus, the total luminous energy falling per second from a standard candle on a square centimeter at a distance of 3 m. is 1 erg. Hence the amount falling per second on a body of the size of an atom, i.e., of cross-section 10^{-15} cm.^{2}, is 10^{-15} ergs, but the energy $h\nu$ with which a corpuscle is ejected by light of wave length 500 $\mu\mu$ (millionths millimeter) is 4×10^{-12} ergs, or 4000 times as much. Since not a third of the incident energy is in wave lengths shorter than 500 $\mu\mu$, a surface of sodium or lithium which is sensitive up to 500 $\mu\mu$ should require, even if all this energy were in one wave length, which it is not, at least 12,000 seconds or 4 hours of illumination by a candle 3 m. away before any of its atoms could have received, all told, enough energy to discharge a corpuscle. Yet the corpuscle is observed to shoot out the instant the light is turned on. It is true that Lord Rayleigh has recently shown that an atom may conceivably absorb wave-energy from a region of the order of magnitude of the square of a wave length of the incident light rather than of the order of its own cross-section. This in no way weakens, however, the cogency of the type of argument just presented, for it is only necessary to apply the same sort of analysis to the case of γ-rays, the wave length of which is of the order of magnitude of an atomic diameter (10^{-8} cm.), and the difficulty is found still more pronounced. Thus, Rutherford estimates that the total γ-ray energy radiated per second by one gramme of radium cannot possibly be more than 4.7×10^4 ergs. Hence at a distance of 100 meters, where the γ-rays from a gramme of radium would be easily detectable, the total γ-ray energy falling per second on a square millimeter of surface, the area of which is ten thousand billion times greater than that either of an atom or of a disc whose radius is

[1] The Electron, 1st edition (1917), pp. 231-3.

a wave length, would be $4.7 \times 10^4 \div 4\pi \times 10^{10} = 4 \times 10^{-7}$ ergs. This is very close to the energy with which β-rays are actually observed to be ejected by these γ-rays, the velocity of ejection being about nine tenths that of light. Although, then, it should take ten thousand billion seconds for the atom to gather in this much energy from the γ-rays, on the basis of classical theory, the β-ray is observed to be ejected with this energy as soon as the radium is put in place."

(3) **Magnitudes of Energy Quanta:** It is of interest to compare, as shown in Table 3.2, the magnitudes of the energy quanta involved in the different types of radiation, and it will be observed that the chief reason for the supremacy of the wave theory of radiation up to 1900 was the fact that the magnitudes of the energy quanta with which physicists were mostly concerned during that period were too small for detection except perhaps by the most sensitive devices. It required, first of all, more refined measurements on the energy distribution in black-body radiation, and following that, the observations on the interaction between radiation (in both the visible and X-ray regions) and electrons in order to bring a realization, on the part of theoretical physicists, that not only is the wave theory inadequate for an interpretation of these effects, but that it is necessary to resort to a theory involving such a strange concept as that of "light darts."

TABLE 3.2

MAGNITUDES OF ENERGY QUANTA

Type of Radiation	Typical Value for λ (cm.)	ν	$h\nu$		
			Erg. atom^{-1}	Cal. mole^{-1}	Volts
Radio waves.......	3×10^4	10^6	6.624×10^{-21}	9.53×10^{-5}	4.14×10^{-9}
Infra-red..........	5×10^{-4}	6×10^{13}	3.97×10^{-13}	5.72×10^3	2.48×10^{-1}
Visible light........	5×10^{-5}	6×10^{14}	3.97×10^{-12}	5.72×10^4	2.48
X-rays...........	1×10^{-8}	3×10^{18}	1.99×10^{-8}	2.86×10^8	1.24×10^4
γ-rays...........	5×10^{-10}	6×10^{19}	3.97×10^{-7}	5.72×10^9	2.48×10^5

Yet, in the measurement of wave length, use is made of the undulatory theory of light. How can the existence of such an apparent dualism in the nature of radiation be interpreted? This was the problem that worried theoretical physicists for a long time and it was only with the discovery of other phenomena, which are discussed in the following sections, that an adequate explanation was developed.

4. COMPTON EFFECT [1]

Other phenomena which have received a simple interpretation in terms of the conception that radiation has an atomistic structure are those connected with scattering of X-rays by free electrons (Compton effect) and the scattering of visible light by molecules (Raman effect).

[1] The most authoritative reference on this topic, as well as on X-rays in general, is ref. C. A.

According to the classical theory, monochromatic light falling on a particle is in general scattered without change of frequency, although under certain special conditions, if the particle or molecule possesses vibration frequencies of its own, a process analogous to modulation in radio may occur.   In 1923, however, A. H. Compton [1] observed that when X-rays impinge on various surfaces, the scattered radiations contain not only some of the same frequency as the incident radiation, but also other radiation of lower frequency, the increase in wave lengths varying according to a definite law with the angle between the primary and scattered X-rays.

In accounting for these observations, Compton found it necessary to treat the X-radiation as constituted of light particles or photons, as he has designated them, possessing not only energy of amount $h\nu$, but also momentum of amount $h\nu/c$.

That electromagnetic radiation possesses momentum follows from the electromagnetic theory of light.   If E designates the amount of energy incident per unit area per unit time on a perfectly absorbing surface, then, according to the wave theory, a pressure is exerted on the surface, of magnitude $P = E/c$.   The existence of this pressure effect was first demonstrated by the classic experiments of Nichols and Hull, and the magnitude shown to be in accord with the theory.

Now on the kinetic theory point of view, the pressure of a gas in an enclosure corresponds to the rate of transfer of momentum per unit area by the molecules incident on the walls.   If, therefore, we assign to the light darts an energy $h\nu$ and let n be the number striking unit area per unit time, then the energy incident per unit area per unit time is $E = n h\nu$, and the pressure is $E/c = n h\nu/c$. That is, the momentum per photon is $h\nu/c$.   Let us then consider on this hypothe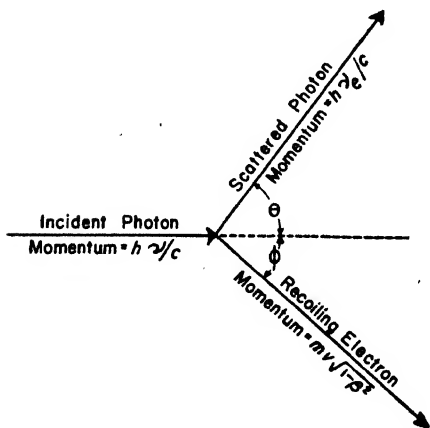sis the collision between a photon and electron.   According to the laws of mechanics, there must exist conservation of momentum as well as of energy.   In Fig. 4.1 [2] the results of such a collision are shown diagrammatically.   The electron suffers a recoil in a direction which makes an angle φ

Fig. 4.1.   Illustrating Theory of Collision Between Photon and Electron

---

[1] *Phys. Rev.*, 21, 207, 483 (1923); 22, 409 (1923) and subsequent papers by A. H. Compton and his students.   See also the following reviews by Compton:

(1) X-rays as a Branch of Optics: *J. Opt. Soc. Am.*, 16, 71 (1928).

(2) The Corpuscular Properties of Light: *Phys. Rev.* (Supplement), 1, 74 (1929).

K. K. Darrow, *Bell. Tech. J.*, 4, No. 2, April 1925; this is an excellent review of the subject.

[2] Ref. C. A., p. 204.

with that of the original direction of motion of the photon, while the photon is scattered in a direction given by the angle θ. Applying the law of conservation of momentum, it follows that the momentum of recoil of the scattering electron must be equal to the vector difference between the momentum of the radiation corresponding to the incident quantum and that of the scattered quantum. The momentum of the electron is given by the expression (derived from the theory of special relativity),

$$\frac{mv}{\sqrt{1 - v^2/c^2}} = \frac{m\beta c}{\sqrt{1 - \beta^2}},$$

where $\beta = v/c$, that is, the ratio of the velocity of recoil of the electron to the velocity of light. Denoting the frequency of the scattered radiation by ν_θ, it follows that

$$\left(\frac{m\beta c}{\sqrt{1 - \beta^2}}\right)^2 = \left(\frac{h\nu_0}{c}\right)^2 + \left(\frac{h\nu_\theta}{c}\right)^2 - 2\frac{h\nu_0}{c} \cdot \frac{h\nu_\theta}{c} \cos \theta. \qquad (4.1)$$

Similarly from the law of conservation of energy, it follows that

$$h\nu_\theta = h\nu_0 - mc^2 \left\{ \frac{1}{\sqrt{1 - \beta^2}} - 1 \right\}, \qquad (4.2)$$

where the second term on the right hand side of the equation gives the kinetic energy of recoil of the scattering electron, on the basis of the special theory of relativity.

Solving these two equations, it is found that

$$\nu_\theta = \frac{\nu_0}{1 + \dfrac{2h\nu_0}{mc^2} \sin^2 (\theta/2)}, \qquad (4.3)$$

or in terms of wave length instead of frequency,

$$\lambda_\theta = \lambda_0 + \frac{2h}{mc} \sin^2 (\theta/2).$$

That is,

$$\lambda_\theta - \lambda_0 = \frac{h}{mc} (1 - \cos \theta). \qquad (4.4)$$

Furthermore the electron recoils from the incident photon at an angle φ given by the relation,

$$\cot \varphi = - (1 + \alpha) \tan (\theta/2), \qquad (4.5)$$

where $\alpha = h/(mc\lambda)$, and the kinetic energy of the recoiling electron is

$$E_k = h\nu \frac{2\alpha \cos^2 \varphi}{(1 + \alpha)^2 - \alpha^2 \cos^2 \varphi}. \qquad (4.6)$$

Substituting in equation (4.4), the values $h = 6.624 \times 10^{-27}$; $m = 9.1065 \times 10^{-28}$, and $c = 2.99776 \times 10^{10}$, this equation shows that the maximum increase in wave length due to the Compton effect, should be $2h/mc = 0.04853\text{Å}$.

Figure 4.2 [1] shows diagrammatically the arrangement used by Compton for measuring the shift in wave length produced in the X-rays proceeding from the molybdenum target T of the tube by the scattering block of graphite located at R. Lead diaphragms prevented stray radiation from leaving the lead box that surrounded the X-ray tube, while the rays, after passing through the slits, were measured by a Bragg spectrometer in the usual manner.
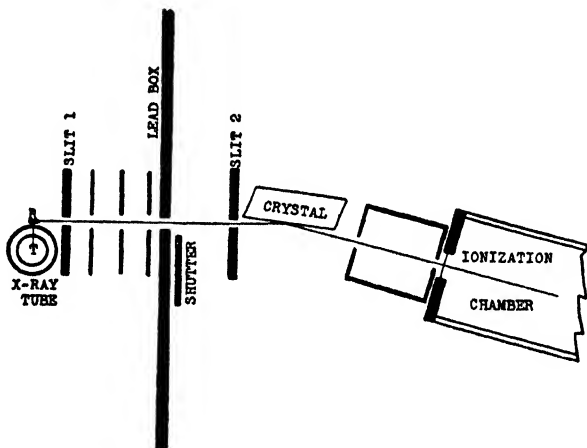

FIG. 4.2.   Arrangement Used for Experiment on Compton Effect

Figure 4.3 shows the results of a series of measurements on the scattering by graphite of the $K\alpha$ line of molybdenum. The line P corresponds in each case to the "unmodified" line (λ_0), while the line at M gives the location of the modified line (λ_θ) as calculated by means of equation (4.4).

A number of investigators have confirmed the general validity of this equation for the "Compton" shift.[2]   As a result of a very careful set of measurements, N. L. Gingrich [3] deduced, on the basis $d = 3.029\text{Å}$, for the grating space of calcite, the value $h/mc = 0.02424$. However, P. A. Ross and P. Kirkpatrick [4] also carried out a series of precision measurements of the Compton shift for ninety degree scattering of three different wave lengths of X-rays, by carbon and beryllium, and found that "in all cases the shift is less than h/mc." They suggested a modification of the Compton equation which takes into account the scattering by *bound* electrons and which leads to an equation of the

[1] Figures 4.2 and 4.3 are taken from *Phys. Rev.*, **22**, 409 (1923).
[2] See ref. C. A., pp. 208–210 for complete list of references to 1935.
[3] *Phys. Rev.*, **36**, 1050 (1930).
[4] *Ibid.*, **45**, 223 (1934); **46**, 668 (1934).

form

$$\Delta\lambda = \Delta\lambda_c - D\lambda^2,$$

where D is a constant for a given scattering material, and $\Delta\lambda_c$ is the shift calculated according to Compton's formula. According to this equation, the latter should be obtained from the observed values of $\Delta\lambda$ by extrapolating to $\lambda = 0$, and in this manner the result obtained was $h/mc = 0.02418$.[1]
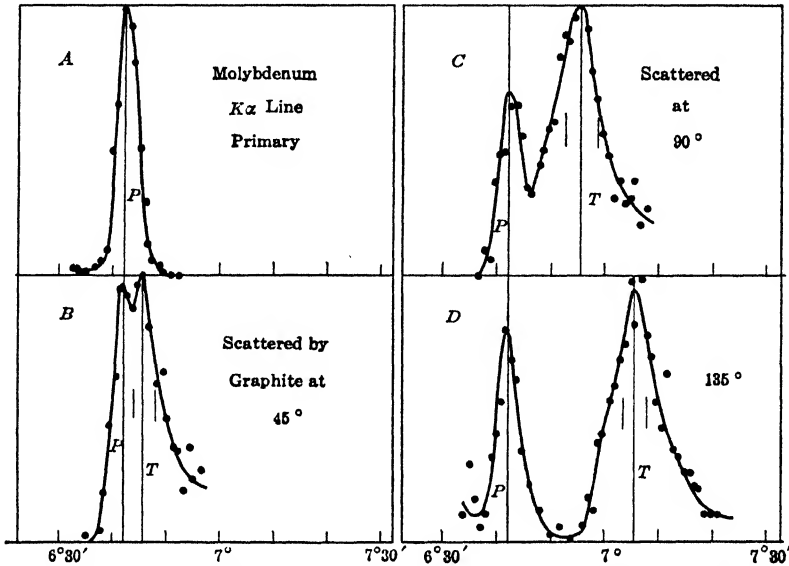

Fig. 4.3. Variation in Wave Length with Angle of Incidence of Secondary Radiation in Compton Effect

Within a short time after Compton's initial publication C. T. R. Wilson [2] demonstrated by means of cloud expansion photographs the presence of the recoil electrons which showed as short tracks pointed in the direction of the incident X-rays, accompanying the much longer tracks due to photoelectrons ejected by the latter. Similar observations were made about the same time by W. Bothe.[3]

A further study by A. H. Compton and A. W. Simon,[4] of the relative numbers of the short and long tracks led to the conclusion, in agreement with the expectation, "that on the average there is about one quantum of energy scattered for each short track that is produced." [5]

[1] For a discussion of the value of this method for the precise determination of h/m, see J. W. M. DuMond, *ibid.*, **56**, 153 (1939).

[2] *Proc. Roy. Soc.*, [**A**], **104**, 1 (1923).

[3] *Z. Physik*, **16**, 319 (1923).

[4] *Phys. Rev.*, **25**, 306 (1925).

[5] A. H. Compton, *J. Franklin Inst.*, **205**, 155 (1928).

According to equation (4.6) the maximum kinetic energy of the recoil electrons, that is the energy of these electrons in the forward direction of the beam of X-rays, should be

$$E_k = mc^2 \frac{2\alpha^2}{1 + 2\alpha} \cdot \qquad (4.7)$$

Measurements of the maximum energy by A. A. Bless,[1] by application of a magnetic deflection method similar to that described in a previous section, were found to be in agreement with this equation.

While all these observations are best interpreted in terms of a photon theory of the nature of radiation, N. Bohr, H. A. Kramers, and J. C. Slater suggested [2] in 1924 that the conservation of energy and conservation of momentum might apply to the photon-electron collision only as statistical laws and not to each individual collision. By means of this hypothesis it might be possible, as they pointed out, still to preserve in certain respects the validity of the electromagnetic theory of energy propagation.

In order to test this idea, W. Bothe and H. Geiger [3] performed an experiment which demonstrated that in the scattering of a photon, the recoil of the electron and that of the modified photon occur *simultaneously.* Furthermore, A. H. Compton and A. W. Simon [4] showed that with *each* recoil electron in the direction of the angle φ there is associated a modified photon which travels in a direction making an angle θ with that of the incident photon, and that these two angles are related in accordance with Compton's equation (4.5).

"We thus find," as Compton and Allison state,[5] "that the wave length of the scattered rays is what it should be if the quantum of radiation bounced from an electron, just as one billiard ball bounces from another. Not only this, but we actually observe the recoiling billiard ball, or electron, from which the quantum has bounced, and we find that it moves just as it should if a quantum had bumped into it. . . .

"Unless the experiments we have been considering have been affected by improbably large experimental errors, there seems to be no escape from the conclusion that the fundamental assumptions on which the photon theory of scattering is based are valid. To be specific, (1) that the incident X-ray beam is divisible into discrete units possessing energy $h\nu$ and momentum $h\nu/c$ and that these units, or photons, may be scattered one at a time in definite directions by individual electrons, and (2) that when a photon is scattered by an electron, energy and momentum are conserved in the process."

In connection with the discussion of this topic it is of interest to point out the reason the Compton effect has not been observed in the scattering of ordinary light by atoms. For this purpose we shall quote from the survey by K. K. Darrow: [6]

[1] *Phys. Rev.*, **30** 871 (1927).

[2] *Phil. Mag.*, **47**, 785 (1924).

[3] *Z. Physik*, **26**, 44 (1924); **32**, 639 (1925).

[4] *Phys. Rev.*, **26**, 289 (1925).

[5] Ref. C. A., pp. 220, 227.

[6] *Bell Tech. J.*, **8**, 64 (1929). This paper gives an excellent review of the Compton and Raman effects.

"If a swiftly moving corpuscle," he points out, "of relatively small mass m strikes a slowly moving body of much larger mass M, the latter cannot gain much speed in the encounter; for it cannot acquire speed without acquiring momentum, and if it were to accept for that purpose more than a very small fraction of the energy of m, it would have to take more momentum than all that m possesses.

"Now relatively to an atom, a corpuscle of light is a body of very small mass and very swift flight indeed; and a quantum of frequency ν cannot transfer to an atom of mass M, for use as kinetic energy of translation, more than the fraction $2h\nu/Mc^2$ of its own initial energy—more than the quantity $2h^2\nu^2/Mc^2$ altogether.[1] For a quantum belonging to the visible spectrum the fraction $2h\nu/Mc^2$ is of the order of 10^{-8} even for an impact with the lightest of all atoms. The utmost possible shift in frequency of the scattered light would bear only this proportion to the primary frequency and would be indistinguishable. But the higher the frequency of the quantum, and the lower the mass of the scattering particle, the greater this maximum possible transfer of energy and this maximum possible frequency-shift become; and for a collision between an X-ray quantum and a free electron, it attains the order 10^{-2} of the primary frequency, and is very appreciable."

5. RAMAN EFFECT

This effect was discovered early in 1928 by C. V. Raman.[2] and may be described briefly as follows: If a substance is irradiated with monochromatic light, scattered light is observed in a direction at right angles to that of the incident beam, as shown in Fig. 5.1.[*] An examination of this emergent light
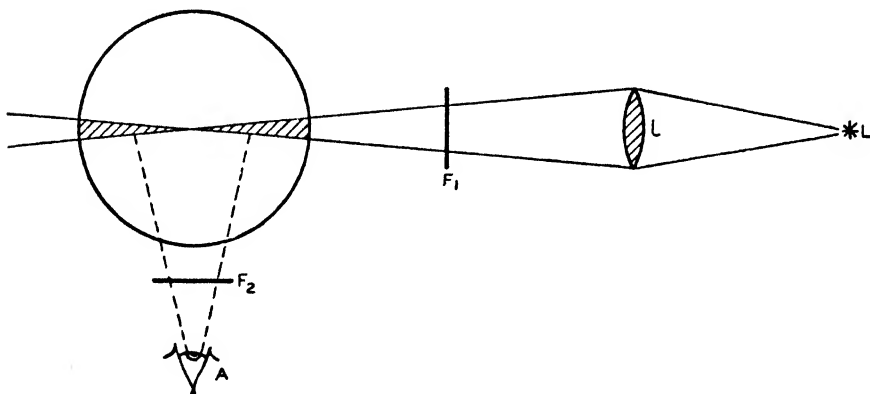

FIG. 5.1. Arrangement for Observation of Raman Effect

by means of a spectrograph shows in general that there has been no change in frequency—an observation which is in agreement with the expectations of classical theory. This is designated as "Rayleigh" scattering and occurs especially if the particles irradiated are of colloidal size. Now what Raman observed was that in addition to this unmodified frequency there were also

[1] This may be deduced directly from equation (4.3).

[2] C. V. Raman, *Indian J. Phys.*, **2**, 1 (1928); C. V. Raman and K. S. Krishnan, *ibid.*, **2**, 339 (1928); *Phys. Rev.*, **33**, 871 (1929).

[*] K. K. Darrow, *Bell Tech. J.*, **8**, 64 (1929).

present lines corresponding to radiation of slightly lower frequencies. Furthermore it was found that the differences in frequency were the same, within the limits of experimental error, as frequencies obtained from infra-red absorption spectra.

Smekal [1] had suggested, in view of the observations on the Compton effect, that in collisions between light quanta and molecules the incident quantum might give up part of its energy to increase the internal energy of the molecule, the remainder being scattered as a quantum of lower energy, or the reverse process might occur. However, the first evidence for the existence of such an effect was obtained by Raman as a result of an investigation on the scattering of some of the mercury lines by a number of liquids.

From the point of view of the quantum theory, we may interpret the Raman effect as follows. A photon of energy $h\nu$ collides with a molecule of the substance irradiated and emerges in general as a photon of lower energy, $h\nu'$, while the difference in energy is converted into increased vibrational energy of the molecule in accordance with the equation,

$$h(\nu - \nu') = h\nu_v, \tag{5.1}$$

where ν_v is a vibrational frequency, which may be observed from the infra-red absorption spectrum. In consequence of the fact that spectral lines arise from transitions between energy states, the frequency ν_v is actually obtained from the difference in energy of two vibrational levels E_1 and E_2 in accordance with the Bohr relation

$$\nu_v = (E_1 - E_2)/h.$$

The significance of such observations for the understanding of atomic interactions in molecules may be illustrated by considering the case of a symmetrical diatomic molecule. In such a molecule the two atoms vibrate with a definite frequency in the direction of the line joining their centers. From the equation for a simple harmonic oscillator it follows that the frequency of vibration is given by the relation *

$$\nu_v = \frac{1}{2\pi} \sqrt{b/m}, \tag{5.2}$$

where m is the mass of each atom, and b the force constant. While a similar mechanical system may assume a continuous range of frequencies, the vibrational energy states of a molecule form a *discrete* series, like the electronic states of an atom. Only, the differences between successive vibrational energy levels are of the order of fractions of a volt, and consequently transitions between these levels are observed as lines in the infra-red region.†

[1] *Naturwiss.*, 11, 873 (1923).

* See further remarks in connection with equation (6.22), p. 183.

† More accurately, the vibrational energy levels are superposed on the electronic levels and in addition there are also present rotational energy levels, the whole system of levels giving rise to the band spectra which are characteristic of molecules.

In the case of polyatomic molecules, each pair of atoms gives rise to a characteristic vibration frequency, so that the spectra of molecules like C_6H_6 or CCl_4 exhibit a number of absorption regions, each one due to a different vibration frequency of the molecule.

From equation (5.2) it is evident that a determination of ν_v gives information regarding the magnitude of b, the interatomic force constant. Thus the observations on the Raman effect furnish a very convenient and more accurate method for the determination of ν_v and b than is possible by means of infra-red absorption measurements.

While, in a previous paragraph it was stated that the modified line in the Raman spectrum corresponds to a frequency ν' lower than the frequency ν of the incident radiation, many cases have been observed in which ν' is greater than ν, indicating that the incident photon has received energy from the molecule as a result of a collision. Such lines are known as "anti-Stokes" lines, because they apparently violate a law enunciated by Stokes, many years previously, that the frequency of the lines produced by excitation of radiation of a given frequency (as in fluorescence) must always be lower than that of the latter. On the basis of the theory discussed above, there is, however, no reason why anti-Stokes lines should not occur.

According to equation (5.1), the difference between the frequency of the incident and that of the scattered light should correspond to a frequency obtained from the infra-red absorption spectrum. Table 5.1 taken from a comprehensive paper by P. Pringsheim and B. Rosen [1] shows a few of the re-

TABLE 5.1

Exciting Line		Modified Line				
λ	$\tilde{\nu}$	λ	$\tilde{\nu}$	$\Delta\tilde{\nu}$	λ_R	λ_A
Å	cm.$^{-1}$	Å	cm.$^{-1}$	cm.$^{-1}$	μ	μ
4359	22,937	4557	21,940	997	10.48	10.3
		4595	21,755	1182	8.45	8.67
		4685	21,340	1597	6.25	6.2
		5029	19,880	3057	3.27	3.25
4348	22,994	4545	21,997	997	10.48	10.3
		4645	21,521	1473	6.79	6.75
4047	24,704	4216	23,713	997	10.48	10.3
		4250	23,520	1184	8.45	8.67
		4324	23,120	1584	6.31	——
		4328	23,100	1604	6.23	6.2
		4619	21,642	3062	3.27	3.25

sults obtained by them with benzene, using the radiations from a mercury arc. The first two columns give the wave lengths (λ) and wave numbers ($\tilde{\nu}$) of the exciting mercury lines; the third and fourth columns give similar data for the

[1] *Z. Physik*, **50**, 741 (1928).

modified lines, the fifth column gives values of $\Delta\tilde{\nu}$, the difference in wave-numbers of exciting and modified lines, while the sixth column gives the corresponding values of the infra-red vibration band ($1\mu = 10^{-4}$ cm.). The last column gives, for comparison, actually observed bands (λ_A) in the infra-red absorption spectrum of benzene. It will be observed that the agreement between the values of λ_R and λ_A is very satisfactory.

R. W. Wood [1] has greatly developed the technique of observations on the Raman effect by using a helium discharge as source of light, since the radiation from this source contains fewer lines in the visible, and the modified lines can therefore be observed more readily.[2]

The Raman effect has also been observed for solids. In fact it was through observations on the scattering of monochromatic radiation by quartz that G. Landsberg and L. Mandelstam [3] were led to the discovery of the effect independently, at about the same time as Raman. In the case of quartz the observed frequency-shifts correspond to infra-red lines of wave lengths 9μ, 13.5μ, 21.5μ, 48μ, and 81μ respectively. The infra-red bands or "Reststrahlen" which have actually been observed are located at 8.7, 12.8 and 20.7μ respectively.

Similar observations have been made by C. Shaefer, F. Matossi and H. Aderhold [4] on Raman spectra obtained by irradiation of crystals such as calcite and aragonite (typical of carbonates), sodium nitrate, sodium bromate, barium sulfate, and ammonium chloride, with mercury lines in the range $\lambda4046.8$ to $\lambda4358.6$. In all cases the change, $\Delta\nu$, in the frequency of the secondary line, corresponded to that calculated from the wave length of an absorption peak observed for the given crystal in the infra-red region.

The Raman effect has also been applied to diatomic and polyatomic gases for the investigation of the different modes of vibration, thus supplementing the results obtained from observations on absorption spectra in the infra-red.[5]

Since the publication of Raman's first papers, the literature on this subject has increased rapidly because of its value in the solution of many problems involving the structure and constitution of different types of molecules, in both inorganic and organic chemistry. It has been stated quite aptly that "the Raman effect began as a step-child of physics, but as time progressed it became the adopted son of chemistry."[6]

[1] R. W. Wood, *Nature*, **122**, 349 (1928); **123**, 279 (1929); *Phil. Mag.*, **6**, 729; **7**, 858 (1929).

[2] The experimental technique is also described by H. L.

[3] *Naturwiss.*, **16**, 557 (1928).

[4] *Z. Physik*, **65**, 289 (1930).

[5] A report on recent work of this nature has been published by G M. Murphy, *J. Opt. Soc. Am.*, **30**, 396 (1940).

[6] J. H. Hibben, *Raman Jubilee Volume, Ind. Acad. Sci.*, p. 294 (1939).

Of the earlier papers on this subject the following are specially worth noting: A. Dadieu and K. W. F. Kohlrausch, *Physik. Z.*, **30**, 384 (1929); Bhagavantam, *Indian J. Phys.*, **5**, 257 (1930); J. H. Hibben, *Chem. Rev.*, **13**, 345 (1933). This comprehensive paper reviews "Raman Spectra in Inorganic Chemistry," and contains a very complete bibliography.

Many of the papers on Raman spectra have been published in *Indian J. Phys.*

6. Quantum Theory of Radiation *

(1) **Black-body Radiation:** As mentioned in the introduction, the quantum theory was originally formulated by M. Planck in 1901, in order to account for observations made by O. Lummer and E. Pringsheim (1879–99), on the radiation emitted by a so-called black body, as a function of both wave length and temperature. In this section we shall therefore discuss the exact nature of these observations and the reasons for the failure to find an interpretation for them on the basis of classical concepts.

With increase in temperature, the energy radiated per unit area per unit time from any surface increases rapidly, and simultaneously the color changes from a dull red through cherry red and orange up to a bright white heat. Furthermore it is observed that at the same temperature, as defined, for instance, by a perfect gas thermometer, the rate of energy emission is much less for a bright metal like platinum, than for a dull black surface, such as an incandescent carbon filament.

During the nineteenth century the subject of radiant energy received considerable attention and as a result certain ideas and relations were developed which are fundamental in any discussion of the topic.

By the *total emissive power* (designated by E) is indicated "the total radiant energy emitted per unit time per unit area of surface of the radiating body." It is measured in terms of erg cm.$^{-2}$ sec.$^{-1}$ or watt cm.$^{-2}$ (1 watt = 10^7 erg sec.$^{-1}$). Table 6.1 shows the variation with T † in the value of E for tungsten (E_W) ‡ and for a "perfect" radiator (E_B). The latter will be defined in the following paragraph.

Comparing the value of E_S at any given temperature for any surface with that for a perfect radiator, E_B, we have the relation

$$E_S = e_t E_B, \qquad (6.1)$$

where e_t is known as the *total emissivity*.

When radiation strikes an opaque surface, part of it is reflected and the rest absorbed. Let A_S designate the *absorptivity*, that is, the fraction ab-

---

* (1) The classical treatise on this subject is, of course, Planck's "Theory of Heat Radiation," translated by P. Massius, P. Blakiston and Son, Philadelphia (1914).

(2) A very comprehensive treatment of the electromagnetic theory, principle of equipartition of energy, and the quantum theory as developed to 1913 is given in the volume by K. Jellinek, Physikalische Chemie der Gasreaktionen, S. Hirzel (1913).

(3) Ref. F. K. R. contains an excellent presentation of fundamental concepts of the theory of radiation and has been used freely by the writer in connection with the discussion in this section.

(4) Ref. H. L. Chapter II contains a very clear exposition of the topic.

† Expressed on the absolute centigrade scale, that is, in degrees Kelvin.

‡ Values of E for tungsten (E_W) are taken from the paper by H. A. Jones and I. Langmuir, *Gen. Elec. Rev.*, **354** (1927). Values of E_B have been calculated by means of the relation deduced in the subsequent discussion, $E_B = 5.6751 \times 10^{-12} T^4$ watts cm.$^{-2}$.

TABLE 6.1

T	Watts/cm.²		
	E_B	E_W	e_t
600	0.736	0.0304	0.041
800	2.33	.169	.073
1000	5.675	.602	.106
1500	28.74	5.52	.192
2000	90.78	24.04	.265
2500	221.6	69.8	.315
3000	459.6	160.5	.349
3500	851.9	318.0	.373
4000	1453		
5000	3548	[M. P. = 3655° K.]	

sorbed.   Then, according to Kirchhoff,

$$\frac{E_S}{A_S} = \frac{E_B}{1} = E_B. \tag{6.2}$$

This law states that at a given temperature, the ratio of emissive power to absorptivity is a constant, independent of the nature of the surface, and equal to the emissive power of a perfect radiator.   Such a radiation may be obtained experimentally from a small opening in a uniformly heated enclosure (hohlraum) and is also approached very closely by a dull black surface, such as that of carbon.   Because of this observation, a surface having an absorptivity of unity is known as a *"black-body"* radiator.   From equations (6.1) and (6.2) it follows that $e_t = A_S$ is a pure number, the value of which may range from 0 (for a perfect reflector) to 1 (for a perfect absorber, or black body radiator). In Table 6.1 the fourth column gives the values of e_t for tungsten, which are obtained from the data in the second and third columns.

About 1879 Stefan concluded [1] from certain measurements of Tyndall that the total energy flux from a radiator varies with the fourth power of the absolute temperature.   This relation is valid only for a black body source, as was deduced subsequently by Boltzmann.[2]   Actually it is observed from graphs of log E versus log T that for most metals the exponent of T is nearer 5.   This arises, of course, from the variation with T of the emissivity, e_t.

In his derivation of the relation between E and T, Boltzmann made use of two concepts: energy density and radiation pressure (p), which are of extreme importance in the theoretical consideration of radiation.

Since radiant energy is propagated in space with finite velocity, it follows that there must be present, in any given volume, a definite amount of energy, that is, there must exist a certain density of radiant energy (designated by ψ)

[1] *Wien. Sitzungsber.*, **79**, 391 (1879).

[2] *Wied. Ann.*, **22, 33,** 291, 616 (1884); M. Planck, *op. cit.*, p. 63.

and this radiation must be in thermal equilibrium with the walls of the hohlraum. A relatively simple calculation [1] shows that

$$\psi = \frac{4}{c} E. \tag{6.3}$$

The existence of radiation density necessarily leads to the conclusion that radiation must exert a pressure. As mentioned in connection with the Compton effect it follows from the electromagnetic theory, and has been demonstrated experimentally,[2] that for a beam of radiation incident normally on a surface the pressure P is given by the relation $P = E/c$, where E is the total amount of energy striking unit area per unit time. On the basis of the quantum theory this leads to the conclusion, confirmed by the observations on the Compton effect that not only is the energy quantized, but also the momentum. We can use this result to derive the relation between energy density and radiation pressure by means of considerations which are quite analogous to those used in the kinetic theory of gases.

Let us consider an enclosure filled with monochromatic radiation of frequency ν, and let n be the number of photons per unit volume.

Hence,

$$\psi = nh\nu. \tag{6.4}$$

The number of photons crossing unit area per unit time in any one direction is

$$n_0 = nc/6. \tag{6.5}$$

Each photon possesses a momentum of magnitude $h\nu/c$, as shown by the Compton effect. Since we are dealing with an enclosure in which the radiation is reflected by the walls, the pressure per unit area, which corresponds to the rate of transfer of momentum per unit area, is given by

$$\begin{aligned} p &= n_0 \cdot 2h\nu/c \\ &= nh\nu/3 \\ &= \psi/3. \end{aligned} \tag{6.6}$$

Extending this conclusion to radiation in a hohlraum at temperature T, we have the relations

$$p = \frac{1}{3} \psi \tag{6.7}$$

$$= \frac{4}{3c} E. \tag{6.8}$$

---

[1] H. L., *op. cit.*, p. 52; F. K. R., *op. cit.*, Ch. VII.
[2] *Phys. Rev.*, **13**, 293 (1901); **17**, 26, 91 (1903); *Ann. Physik*, **12**, 225 (1903).

This relation which is derived more rigorously from the electromagnetic theory of light was used by L. Boltzmann [1] to show, by means of a thermo-dynamical cycle process, that the radiation density must vary with temperature in accordance with the relation

$$\psi = aT^4. \tag{6.9}$$

Combining this with equation (6.3), it follows that

$$E = \frac{c}{4}\psi = \frac{ca}{4}T^4$$
$$= \sigma T^4. \tag{6.10}$$

A considerable number of determinations have been published of the value of σ, the "Stefan-Boltzmann" constant.[2] These have been examined critically by R. T. Birge [3] and more recently by F. G. Dunnington [4] and H. T. Wensel.[5] According to the latter the (unweighted) average of all the values from about 1900 to 1929 is

$$10^5\,\sigma = 5.69 \text{ erg cm.}^{-2} \text{ sec.}^{-1} \text{ deg.}^{-4}.$$

The weighted average values deduced by Birge and Wensel are 5.735 and 5.775 respectively.

On the other hand, as will be shown in a subsequent section, the quantum theory of radiation leads to an expression for σ, of the form

$$\sigma = \frac{2\pi^5 k^4}{15c^2 h^3}.$$

Substituting the values for the constants given in Table B of the Appendix, the result is

$$\sigma = 5.6751 \times 10^{-5} \text{ erg cm.}^{-2} \text{ sec.}^{-1} \text{ deg.}^{-4}$$
$$= 5.6751 \times 10^{-12} \text{ watt cm.}^{-2} \text{ deg.}^{-4}$$

This is the value which has been used in calculating values of E_B given in Table 6.1.

From this it follows that the constant a in equation (6.9) has the value

$$a = \frac{4\sigma}{c} = 7.572 \times 10^{-15} \text{ erg cm.}^{-3} \text{ deg.}^{-4}$$

[1] *Wied. Ann.*, **22**, 33, 291, 616 (1884); also ref. F. K. R.

[2] A very complete list of these values is given by H. T. Wensel, *J. Res. Nat. Bur. Stand.*, **22**, 375 (1939).

[3] *Phys. Rev.* (Supplement), **1**, 1 (1929).

[4] *Rev. Mod. Phys.*, **11**, 65 (1939).

[5] *Loc. cit.*

(2) **Spectral Distribution of Black-Body Radiation**: During the period 1897–1901, Lummer and Pringsheim investigated the spectral distribution of black-body radiation for a series of temperatures.

Their results are shown in Fig. 6.1. The ordinates correspond to *emissive power per unit wave length interval* and the abscissae indicate the wave lengths in terms of microns ($1 \mu = 10^{-4}$ cm.).

These curves show that at 723° K, the wave length having the maximum energy is 4.08μ, but there is sufficient energy even at 0.76μ or slightly lower wave lengths to affect the eye. Thus, a body at this temperature shows a red color. As the temperature increases above 723° K, the position of the maximum is continually shifted towards shorter wave lengths until, at 1646° K, it is at wave length 1.78μ. At the same time, as the intensity of the energy in the shorter wave lengths increases, the color of the radiation varies from red through cherry red and orange up to a bright white heat.

Intensity of Radiation: For the proper understanding of the laws of black-body radiation, it is necessary to examine further the physical significance of the energy distribution curves shown in Fig. 6.1.

The total energy E is composed of radiations of wave lengths varying from $\lambda = 0$ to $\lambda = \infty$.

Fig. 6.1. Energy Distribution for Black-Body Radiation

Furthermore, the intensity of each of these monochromatic radiations which constitute the total radiation is not the same. If we denote the monochromatic emissive power corresponding to wave length λ by E_λ, we obtain the obvious relation

$$E = \int_0^\infty E_\lambda d\lambda. \tag{6.11}$$

We may therefore define E_λ as "the radiant energy (of wave length λ) per unit wave-length interval emitted per unit time by unit area of a black body throughout the solid angle, 2π, i.e., hemispherical radiation," [1] and $E_\lambda d\lambda$ represents the *energy flux* per unit area for a spectral region between λ and $\lambda + d\lambda$. This is the physical significance of the ordinates used in Fig. 6.1. The total energy radiated per unit time per unit area at any given temperature is given by the area under the corresponding spectral distribution curve.

Corresponding to E_λ, there exists a specific *intensity of radiation*, K_λ, characteristic of the surface, and it may be shown from very simple consider-
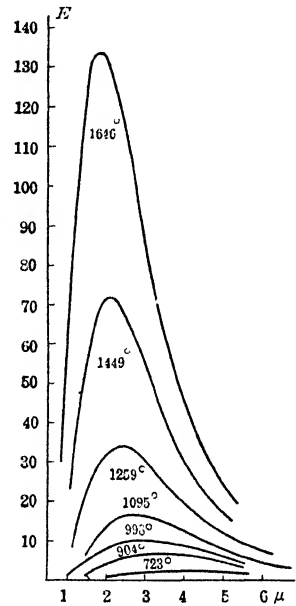
[1] Wensel, *loc. cit.*

ations [1] that

$$E_\lambda = \pi K_\lambda. \tag{6.12}$$

Thus K_λ corresponds to what is known as "brightness" of a surface in photometry.

If instead of the energy distribution with respect to wave length, we consider the distribution curve with respect to frequency, then

$$E = \int_0^\infty E_\nu d\nu. \tag{6.13}$$

In consequence of the relation $\nu\lambda = c$, it follows that

$$d\nu = -\frac{c}{\lambda^2} d\lambda \tag{6.14a}$$

and $\qquad E_\lambda = \frac{c}{\lambda^2} E_\nu. \tag{6.14b*}$

Also, corresponding to K_λ, we have the relation

$$E_\nu = \pi K_\nu.$$

To describe the observations of Lummer and Pringsheim at least two equations were suggested which are of theoretical importance. One of these was deduced by Wien, the other by Rayleigh and Jeans. Since neither of these equations was found to be satisfactory, a way out of the difficulty was found by Planck through the quantum hypothesis.

(3) **Wien's Radiation Law:** In deriving his equation, W. Wien [2] assumed the following cycle: Imagine the black-body enclosure filled with radiation at a certain temperature to be provided with a movable piston. The radiation will exert a pressure on the piston according to equation (6.7). We now perform a cyclic process in which the radiation is expanded adiabatically and then compressed very slowly. Taking into account the fact that, according to Doppler's principle, the color of any monochromatic radiation (that is, the frequency) is altered by reflection from a moving surface, and applying the second law of thermodynamics, it follows that

$$E_\nu = \frac{\nu^3}{c^2} F\left(\frac{\nu}{T}\right), \tag{6.15}$$

where the form of the function F still remains undetermined.

It follows from the last equation that, as the temperature increases, the frequency (ν_m) at which E_ν has the maximum value varies directly as the

---

[1] Ref. F. K. R.

* The negative sign is omitted because it is of no physical significance in this case.

[2] *Wied. Ann.*, **52**, 132 (1894).

absolute temperature. That is,

$$\nu_m = \text{const.} \times T$$
$$\text{and} \qquad \lambda_m = \frac{A}{T}, \tag{6.16}$$

where A is a constant which has the observed value 0.290 cm. deg. (approx.). Hence, for $\lambda_m = 0.55 \mu$ (the wave length for which the human eye is most sensitive), $T = 5270°$ K approximately. This would, therefore, be the temperature at which a black-body radiator would emit light of the same distribution as is actually emitted by the sun at a somewhat higher temperature (about 6000° K).

By making use of equation (6.14b), equation (6.15) may evidently be expressed in the form

$$E_\lambda = \frac{c^2}{\lambda^5} F\left(\frac{c}{\lambda T}\right). \tag{6.17}$$

Combining this relation with equation (6.16) and differentiating, it follows that

$$E_{\lambda_m} = BT^5. \tag{6.18}$$

That is, the maximum value of E_λ for a black-body radiator varies as the fifth power of the absolute temperature.

Equations (6.15) and (6.17) represent alternative formulations of Wien's Displacement Law, and equations (6.16) and (6.18) are two important corollaries of the law which have been very amply confirmed by experimental observation. The values of the constants A and B are discussed in a subsequent section.

The next problem that presented itself was the determination of the function F. In order to accomplish this, Wien introduced two additional assumptions of a questionable nature regarding the mechanism of radiation and deduced the relation

$$E_\nu = \frac{\alpha \nu^3}{c^2} e^{-(\beta \nu / T)},$$

where α and β are constants. Expressed in terms of wave lengths, this relation becomes

$$E_\lambda = \left(\frac{c_1}{\lambda^5}\right) e^{-(c_2/\lambda T)}. \tag{6.19}$$

This form of Wien's Radiation Law is the one most generally used and c_1 and c_2 are referred to as the constants in Wien's equation.[1]

---

[1] A complete discussion of Wien's equation and a comparison with the data of Lummer and Pringsheim are given by W. Wien and O. Lummer in *Rapports du congrés international physique*, **2**, 23–99 (1900).

A comparison of this equation with the measurements of Lummer and Pringsheim showed, however, that there is agreement only for low values of λT. Thus Wien's equation is perfectly satisfactory for frequencies in the visible and ultra-violet regions, even at the highest temperature, but fails completely when applied to heat waves and radiations of longer wave length.

On the other hand, Lord Rayleigh and Jeans, basing their arguments on the classical theory, derived a distribution law which has been found to be in agreement with the observations for large values of λT (that is, longer wave lengths) but breaks down completely when applied to the spectral region in which Wien's equation is valid. Since the Rayleigh-Jeans equation involves no additional assumptions except that of the validity of Newtonian dynamics when applied to radiation, it is necessary to discuss the fundamental principle on which this equation was based. This is all the more essential because the quantum theory represents a complete severance from this apparently well-founded principle which is known as that of the equipartition of energy.

(4) **Principle of Equipartition of Energy:** [1] According to the kinetic theory of gases, the average kinetic energy E_k of the molecules of a gas at any temperature T is given as

$$E_k = \frac{3RT}{2N} = \tfrac{3}{2}kT, \tag{6.20}$$

where N = the Avogadro constant, k = the Boltzmann constant, and R = gas constant per mole.

The direction of the motion corresponding to this translational energy can be represented by three space-coordinates, and if $\dfrac{dx}{dt}$, $\dfrac{dy}{dt}$, and $\dfrac{dz}{dt}$ represent the velocity-components along the three rectangular coordinates, the average kinetic energy of motion is given by the relation

$$\tfrac{3}{2}kT = \tfrac{1}{2}mv^2 = \tfrac{1}{2}m\left\{ \left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2 + \left(\frac{dz}{dt}\right)^2 \right\},$$

where v is the velocity along the direction of motion, and m is the mass of the molecule. It is evident that, in a mass of gas, the average kinetic energy along each of the three coordinates must be the same. Thus, we arrive at the conclusion that the average kinetic energy of a molecule is $\tfrac{1}{2}kT$ for each of the three directions in which it can move.

This conclusion represents a special application of a very general principle, due to the theoretical work of Boltzmann and Maxwell, which is known as the *Principle of Equipartition of Energy*, and which may be stated in the following manner.

[1] A comprehensive discussion of the theoretical consideration on which this principle is based will be found in the following: E. H. Kennard, Kinetic Theory of Gases, McGraw-Hill Book Company, New York (1938); R. C. Tolman, Statistical Mechanics, Chemical Catalog Company, New York; L. Page, Introduction to Theoretical Physics, D. Van Nostrand Co., Inc., New York.

Let q_1, q_2, $\cdots$, q_i, $\cdots$, q_n denote the minimum number (n) of coordinates (such as x, y, z, in the previous illustration) required to represent that state of an atom, or molecule at any instant, and let p_1, p_2, $\cdots$, p_i, $\cdots$, p_n denote the corresponding momenta, where p_i is a generalized momentum of the same nature as $m(dx/dt)$ in ordinary translational motion in one direction. If the total energy, which is the sum of kinetic and potential, can be represented as the sum of a series of quadratic terms of coordinates and momenta of the form:

$$E = \tfrac{1}{2} \sum_1^n \alpha_i q_i{}^2 + \tfrac{1}{2} \sum_1^n \beta_i p_i{}^2,$$

$$\text{(potential)} \qquad \text{(kinetic)}$$

then the average value of the total energy of the system will be given by $E = nkT$, or $kT/2$ *for each term in the above expression.* Hence, if n denote the total number of degrees of freedom, that is, independent terms or parameters required to describe the total kinetic energy of the system, then the average value of the kinetic energy will be $kT/2$ for each degree of freedom. Furthermore for every term in the expression for the potential energy which can be represented in the form $\tfrac{1}{2}\alpha_i q_i{}^2$ (as for instance is the case when q_i is a displacement with an elastic force which obeys Hooke's law) the average potential energy for each such term will also be $kT/2$.

A special case of this nature is the linear harmonic oscillator for which the total energy is represented by the relation

$$E = \frac{p^2}{2m} + \frac{bq^2}{2}, \tag{6.21}$$

$$\begin{aligned}
\text{where} \quad p &= mv = \text{momentum}, \\
q &= \text{displacement}, \\
bq &= \text{restoring force}, \\
\text{and} \quad \nu &= \text{frequency of vibration} \\
&= \frac{1}{2\pi} \sqrt{\frac{b}{m}}.
\end{aligned} \tag{6.22}$$

On the basis of the principle of equipartition the average kinetic energy of such a system is $\tfrac{1}{2}kT$ and since the average value of the potential energy is equal to the average value of the kinetic energy, the total energy is kT.

Now let us consider the bearing of this conclusion on the problem of specific heat of gases. If in the case of a monatomic gas we assume that the only effect of an increase in the temperature of a mass of the gas maintained at constant volume is to increase the kinetic energy of agitation of the molecules, then the heat capacity per mole at constant volume (C_v) ought to be $\tfrac{3}{2}Nk = \tfrac{3}{2}R$, that is, 2.98 calories/mole. Furthermore, in the case of any "perfect" gas, the energy absorbed per mole in expanding at constant pressure is R calories per degree. Consequently the specific heat at constant pressure (C_p) for a monatomic gas ought to be $\tfrac{5}{2}R$. These deductions have actually been found to be

valid and the conclusion is therefore drawn that any rotational energy which the molecules of a monatomic gas may possess is of no importance in regard to the heat capacity.

In the case of diatomic gases, Boltzmann considered the molecule as having a dumbbell sort of structure, with fixed distance between the atoms. On collisions with other molecules it is assumed that the atoms are set in rotation about an axis passing through the center of the line joining them. To describe this rotation requires two coordinates, viz., the inclination of the axis of the dumbbell to that of rotation and the angular velocity about the axis of rotation. Hence, a diatomic molecule should possess altogether five degrees of freedom, three to describe the translational motion of the molecule as a whole and two to correspond to the rotation of the atoms. It follows that the heat capacity per gram-molecule of a diatomic gas, at constant volume, ought to be $\frac{5}{2}R$ and that at constant volume, $\frac{7}{2}R$. This deduction was again found to be in agreement with experimental data, at least at ordinary temperatures.

Not only was Boltzmann able in this manner to calculate the specific heats of gases, but he applied the same considerations to solids and thus arrived at an explanation of the Dulong and Petit law. According to this law the product of specific heat and atomic weight in the case of elements in the solid state is a constant which has a value of about 6 calories. This law was derived empirically at the beginning of the nineteenth century; but until Boltzmann enunciated his theory, there appeared to be no reasonable explanation of such a relation. His argument was to this effect: [1]

Consider an elementary substance in the solid state in equilibrium with its vapor. Assume for the sake of simplicity that the vapor is monatomic. We know that this is actually true in the case of metals like mercury, zinc and cadmium, whose densities in the vapor state have been measured. Now the energy of the atom in the solid state must depend upon the vibration of this atom about a position of equilibrium. It also follows from the principles of dynamics that, in the case of any such harmonic oscillator as that defined in equation (6.21), the average kinetic energy is equal to the average potential energy. But it is evident that the only conditions under which thermal equilibrium can exist between the atoms in the solid phase and those in the gas is that the average kinetic energy of the atom in each state should be the same, and, since the average energy of an atom in the gas is $\frac{3}{2}kT$, it follows that the total energy per atom in the solid is $3kT$, or $3RT$ per gram atom. Consequently the atomic heat should be $3R$, that is, 5.96 calories.

(5) **Rayleigh-Jeans Distribution Law:** In order to apply the principle of equipartition to radiant energy, it is necessary to determine the number of degrees of freedom which have to be assigned to electromagnetic waves. [2]

The ideas used in this case may be understood better by applying them to sound vibrations. For a string fastened at both ends the different modes of

---

[1] See also K. Jellinek, *Gasreaktionen*, p. 368.

[2] A very clear exposition of the argument developed in this section has been given by J. Rice, *Trans. Faraday Soc.*, 11, 1 (1915).

vibration are determined in accordance with the relation which states that one-half the wave length must be an integral submultiple of the length of the string. Denoting the latter by L and the wave length of the stationary wave by λ, we have the relation

$$\frac{n\lambda_n}{2} = L, \tag{6.23}$$

that is,

$$\nu_n = \frac{nu}{2L}, \tag{6.24}$$

where u is the "phase" velocity * of the wave-motion, ν_n is the frequency corresponding to λ_n, and n has the values 1, 2, 3, $\cdots$, associated with the different so-called harmonics of the fundamental $(n = 1)$ tone.

Writing equation (6.23) in the form

$$n = \frac{2L}{\lambda}, \tag{6.25}$$

it is seen that for *very large values* of n,

$$\Delta n = 2L \frac{\Delta\lambda}{\lambda^2}, \tag{6.26}$$

which expresses the relation between the change in wave length and the corresponding change in number of modes of vibration.

Since the vibrations are transverse, two coordinates (those at right angles to the direction of L) are required to define the instantaneous position of any segment of the string. There are therefore two degrees of freedom associated with each mode of vibration, and it follows from equation (6.26) that the number of degrees of freedom (f) per unit length of string in the wave length range λ to $\lambda - \Delta\lambda$ is given by the relation

$$f = 4\Delta\lambda/\lambda^2. \tag{6.27}$$

Let us now consider the possible number of modes of vibration of a two-dimensional system, such as a square metal plate. The condition for a steady state of vibration is that the total number of nodes or loops measured along each side shall be an integral value. Let L denote the side of the square, let n_1 denote the number of loops along one side, and n_2, the same for the side at right angles to the first one. This state of vibration will correspond to a set of stationary waves whose nodal lines are all parallel and inclined to one side of the square at an angle θ_1, and to the adjacent side at an angle θ_2. Hence,

$$\cos^2 \theta_1 + \cos^2 \theta_2 = 1. \tag{6.28}$$

* See discussion in Section 8(2).

Furthermore if d_1 and d_2 designate the projections of $\lambda/2$ (the distance between two successive nodal lines), then the condition for the occurrence of stationary waves is that the following relations shall be valid *simultaneously:*

$$\left.\begin{aligned} d_1 &= \frac{L}{n_1} = \frac{\lambda}{2 \cos \theta_1} \\ d_2 &= \frac{L}{n_2} = \frac{\lambda}{2 \cos \theta_2} \end{aligned}\right\} \quad . \tag{6.29}$$

Combining these two sets of relations with equation (6.28) it follows that,

$$n_1{}^2 + n_2{}^2 = \left(\frac{2L}{\lambda}\right)^2 = \left(\frac{2L\nu}{u}\right)^2 , \tag{6.30}$$

where ν is the frequency, and u, the phase velocity.

If we choose a rectangular system of coordinates and let n_1 and n_2 represent distances along each of these coordinates respectively, then any pair of values of n_1 and n_2 satisfying equation (6.30) corresponds to a point on the circumference of a circle of radius $2L\nu/u$ drawn with its center at the origin. Moreover, all the values of these integers which correspond to positive values of n_1 and n_2 are located in the positive quadrant of the circle.

From these considerations it follows that the *total number of possible modes of vibration* (N), with frequencies between $\nu = 0$ and $\nu = \nu_m$, is given by the *area of a quadrant* of the circle. That is,

$$N = \frac{\pi}{4}\left(\frac{2L\nu_m}{u}\right)^2 = \frac{\pi L^2 \nu_m{}^2}{u^2}$$

and the *number per unit area* of the square with frequencies between ν and $\nu + d\nu$ is given by

$$\frac{dN}{L^2} = \frac{2\pi\nu}{u^2} \, d\nu. \tag{6.31}$$

The argument for the case of a three-dimensional vibrating system is quite similar. The condition for the occurrence of stationary waves in a cube of side L is that the following three relations shall be valid simultaneously:

$$n_1 = \frac{2L}{\lambda} \cos \theta_1,$$

$$n_2 = \frac{2L}{\lambda} \cos \theta_2,$$

$$n_3 = \frac{2L}{\lambda} \cos \theta_3,$$

where $\cos^2 \theta_1 + \cos^2 \theta_2 + \cos^2 \theta_3 = 1.$

Hence

$$n_1{}^2 + n_2{}^2 + n_3{}^2 = \left(\frac{2L}{\lambda}\right)^2 = \left(\frac{2L\nu}{u}\right)^2$$

and the total number of possible modes of vibration (N), with frequencies between $\nu = 0$ and $\nu = \nu_m$, correspond to one-eighth of the volume of a sphere of radius ($2L\nu/u$).   That is,

$$N = \tfrac{1}{8} \cdot \tfrac{4}{3}\pi \left(\frac{2L\nu}{u}\right)^3$$

and

$$\frac{dN}{L^3} = \frac{4\pi\nu^2}{u^3}\,d\nu. \tag{6.32}$$

In applying these conclusions to radiation it is necessary to take into account the fact that light waves have two directions of polarization which are at right angles to each other, and that consequently the number of modes of vibration in the case of electromagnetic waves is *twice* that deduced in equation (6.32).

We thus derive the conclusion that for radiation in a hohlraum the number of degrees of freedom per unit volume, associated with the range of frequencies between ν and $\nu + d\nu$ is given by

$$df = \frac{8\pi\nu^2}{c^3}\,d\nu, \tag{6.33}$$

where c, the velocity of light, is used instead of u in equation (6.32).

We now bring in the principle of equipartition of energy, and postulate that each frequency in the radiation is associated with the vibration of a linear harmonic oscillator, similar to that used in the production of Hertzian waves but of molecular dimensions, so that the frequencies of harmonic vibrations emitted are of the order of magnitude of those present in black-body radiation. Since the whole system of oscillators and waves is in thermal equilibrium, the average energy per oscillator must be kT.   Consequently, the energy per unit volume associated with df degrees of freedom is

$$\psi_\nu d\nu = kT\,df = \frac{8\pi\nu^2 kT}{c^3}\,d\nu \tag{6.34}$$

and, in accordance with equation (6.3), it follows that

$$E_\nu d\nu = \frac{c}{4}\,\psi_\nu d\nu = \frac{2\pi\nu^2 kT}{c^2}\,d\nu. \tag{6.35}$$

Applying equation (6.14b) this may also be written in the form

$$E_\lambda d\lambda = \frac{2\pi ckT}{\lambda^4}\,d\lambda. \tag{6.36}$$

Equations (6.35) and (6.36) represent two alternative expressions of the Rayleigh-Jeans law for the spectral distribution of energy emitted by a black-body source. This law leads to the conclusion that at any given temperature the intensity of radiation should increase with decrease in wave length and ultimately become infinitely great as λ tends to zero. This is evidently not in accord with the observations of Lummer and Pringsheim which indicate that with decrease in λ from the far infra-red into the visible, E_λ increases at first, reaches a maximum and then decreases rapidly in the ultra-violet region. Furthermore, it also follows from equation (6.35), since

$$E = \int_0^\infty E_\nu d\nu, \tag{6.13}$$

that at any temperature E should become infinitely great, whereas thermo-dynamical considerations, verified by experimental observations, lead to the Stefan-Boltzmann law.

On the other hand, it is observed that for large values of λ (the infra-red region) the variation in E_λ with λ is in accordance with the law of Rayleigh and Jeans. That is, equation (6.36) applies to large values of λT, but not to low values of this quantity. Yet, if the principle of equipartition of energy is valid, there is no evident reason why equation (6.35) or (6.36) should not be equally valid for *the whole* range of values of λT.

This difficulty into which we are led by the Rayleigh-Jeans law has been described by Jeans thus:

"Assuming for the moment," he states,[1] "the truth of this as an experimental fact, we may try to illustrate its physical bearings. To make the question as definite and as simple as possible, let us fix our attention on an enclosure with perfectly reflecting walls in which there is a mass of, say, iron at 0° C., and let us suppose that there is a state of equilibrium inside this enclosure. The iron is continually radiating energy out from its surface into the surrounding ether inside the enclosure, and is also absorbing energy from the ether. From the condition of equilibrium, the rates of exchange must just balance. If we assume, for additional simplicity, that the iron is coated with a perfectly absorbing paint, then in point of fact each square centimeter of surface emits 3×10^5 ergs of radiation per second into the ether; and also absorbs 3×10^5 ergs per second of radiation falling on to it from the ether. The energy in the ether is of density 4×10^{-5} ergs per cubic centimeter; the heat energy in the iron is of the order of 8×10^9 ergs per cubic centimeter. The heat energy of the iron resides in the oscillations of its atoms, each atom moving with an average velocity of about 30,000 cms. per second.

"A very little consideration will show that this state of things is different from what might be expected by analogy from other systems which are known to obey the ordinary dynamical laws. Consider, for instance, a tank of water (to represent the ether) in which is floated a system of corks (to represent atoms of matter) connected by light springs or elastics so that they can oscillate relatively to one another. Suppose that initially the surface of the water is at rest. Let the system of corks be set into violent oscillation and placed on the surface of the water. The motion of the corks will set up waves in the water, and these waves will spread all over the surface of the water, undergoing reflection when they meet the walls of the tank. We know that ultimately the corks will be reduced to rest; the energy of their

[1] Report on Radiation and the Quantum Theory, London, 1914.

motion will be transformed first into the energy of waves and ripples on the surface of the water, and then, owing to the viscosity of the water, into heat energy in the water. A final state in which the corks continue to oscillate with extreme vigor while the water has almost no energy is unthinkable; we expect a final state in which practically all the energy has found its way into the water."

In a similar manner we find that "in all known media there is a tendency for the energy of any systems moving in the medium to be transferred to the medium and ultimately to be found, when a steady state has been reached, in the shortest vibrations of which the medium is capable. This tendency can be shown to be a direct consequence of the Newtonian laws. This tendency is not observed in the crucial phenomenon of radiation; the inference is that the radiation phenomenon is determined by laws other than the Newtonian laws."

(6) **Planck's Distribution Law. Quantum Hypothesis:** The failure of both the Rayleigh and Wien equations to account for experimental data showed conclusively that ordinary methods were not applicable in attacking this problem. Since, however, the method of reasoning adopted in arriving at the Rayleigh equation was perfectly logical, the only conclusion to be drawn was that the fundamental principles upon which the argument was based are not of as general validity as supposed.

Now for a number of years a gradually increasing number of facts had led many physicists to question the general validity of the principle of equipartition of energy. For one thing, while the law of Dulong and Petit is pretty generally true, the number of exceptions to it had been accumulating during the past century. Thus, it was known that carbon, boron, and silicon have atomic heats lower than 6; but it was also observed that the atomic heats of these elements increase with temperature, and at high enough temperatures they behave "normally." Furthermore, the molecular heats of some diatomic gases like chlorine and bromine are nearly a calorie too high even at ordinary temperatures, and they become even greater at higher temperatures.

To explain these facts it would be necessary to assume that the number of degrees of freedom of a carbon atom or chlorine molecule increases gradually with the temperature. But the Boltzmann concept leaves no room for such a transition stage. An atom or molecule must possess a certain integral number of degrees of freedom; a degree of movability in any definite manner is either absent or present. There can be no *gradual acquisition* by any body of a degree of freedom. The conception of integral degrees of freedom thus presents many difficulties. Furthermore, it has been shown above that, in the realm of radiant phenomena, similar difficulties are present. The principle of equipartition of energy cannot, therefore, be of as general validity as hitherto assumed. But this principle was deduced from the fundamental laws of dynamics, and is, therefore, just as valid as the latter. Here then was a Gordian knot that appeared as difficult to untie as the one of classical fame. It remained for Planck to apply to this case a similar remedy.

Instead of accepting this principle, Planck introduces the assumption that a harmonic oscillator (of the nature postulated in the previous section) cannot *take up or emit energy continuously, but discontinuously in multiples of a unit quantum of magnitude δ.* That is, the energy of any one oscillator can have one

of the series of values, δ, 2δ, $\cdots$, $n\delta$, where $n\delta$ approximates more and more to kT with increase in n.

The next problem is this: what is the probability that at any temperature T the energy of any given oscillator will have the value $n\delta$? The answer is given by a law deduced by Boltzmann on the basis of statistical mechanics. This law may be stated as follows:

Given an extremely large number of linear harmonic oscillators at a temperature T, the probability that any one oscillator will have the energy $n\delta$, is given by the relation

$$p_n = e^{-n\delta/kT}, \qquad (6.37)$$

where k is the Boltzmann constant.

This therefore represents the relative number of oscillators per unit volume in the hohlraum which possess the energy $n\delta$. If we designate the concentration of oscillators corresponding to $\delta = 0$ by N_0 and that corresponding to $n\delta$ by N_n, equation (6.37) leads to the relation

$$N_n = N_0 e^{-n\delta/kT}. \qquad (6.38)$$

The total number of oscillators per unit volume is given by

$$N = \sum_{n=0}^{\infty} N_n = N_0(1 + e^{-\delta/kT} + e^{-2\delta/kT} + e^{-3\delta/kT} + \cdots)$$

$$= \frac{N_0}{1 - e^{-\delta/kT}}. \qquad (6.39)$$

The total energy per unit volume is

$$\psi = \sum_{n=0}^{\infty} N_n n\delta = N_0(0 + \delta e^{-\delta/kT} + 2\delta e^{-2\delta/kT} + 3\delta e^{-3\delta/kT} + \cdots)$$

$$= N_0 \delta e^{-\delta/kT}(1 + 2x + 3x^2 + \cdots),$$

where

$$x = e^{-\delta/kT}.$$

Since $x < 1$, the series on the right-hand side of the last equation has the value $(1 - x)^{-2}$. Hence

$$\sum_{n=0}^{n} N_n n\delta = \frac{N_0 \delta e^{-\delta/kT}}{(1 - e^{-\delta/kT})^2}. \qquad (6.40)$$

The *average energy*, η, per oscillator is

$$\eta = \frac{\psi}{N} = \frac{\delta e^{-\delta/kT}}{1 - e^{-\delta/kT}} = \frac{\delta}{e^{\delta/kT} - 1}. \qquad (6.41)$$

Since, for $x < 1$,

$$e^x = 1 + x + x^2 + \cdots$$

it follows that for $\delta \to 0$, $\eta \to kT$. That is, as δ becomes vanishingly small, η approaches the classical value.

If now the conclusion stated in equation (6.41) is combined with the value of df in equation (6.33) and the relation for E_ν in equation (6.35), the result is a spectral distribution relation of the form

$$E_\nu d\nu = \frac{2\pi\nu^2}{c^2} \cdot \frac{\delta}{e^{\delta/kT} - 1} \, d\nu. \tag{6.42}$$

Comparing this with equation (6.15) deduced by Wien it follows that δ must be proportional to ν, and Planck therefore assumes

$$\delta = h\nu. \tag{6.43}$$

Accordingly equation (6.42) takes the form,

$$E_\nu d\nu = \frac{2\pi h\nu^3}{c^2} \cdot \frac{1}{e^{h\nu/kT} - 1} \, d\nu \tag{6.44}$$

and the corresponding equation for E_λ is

$$E_\lambda d\lambda = \frac{2\pi c^2 h \lambda^{-5}}{e^{ch/k\lambda T} - 1} \, d\lambda \tag{6.45}$$

$$= \frac{c_1 \lambda^{-5}}{e^{c_2/\lambda T} - 1} \, d\lambda, \tag{6.46}$$

where

$$c_1 = 2\pi c^2 h, \tag{6.47}$$

$$c_2 = ch/k. \tag{6.48}$$

Equation (6.46) is in excellent agreement with all the observations on the spectral distribution law for black-body radiation, and the values of the "radiation constants" c_1 and c_2 so observed, are in very good agreement, as will be pointed out subsequently, with those calculated by means of the last two equations.

For $ch/k > \lambda T$, the exponential factor in the denominator of equation (6.45) is very large compared to unity, and consequently this equation assumes the form,

$$E_\lambda d\lambda = c_1 \lambda^{-5} e^{-(c_2/\lambda T)} d\lambda,$$

which is identical with equation (6.19) for Wien's radiation law.

For $\lambda T \gg ch/k$, the exponential factor

$$e^{c_2/\lambda T} = 1 + c_2/\lambda T$$

and

$$E_\lambda d\lambda = (c_1/c_2)\lambda^{-5} \cdot \lambda T d\lambda$$
$$= 2\pi ckT\lambda^{-4} d\lambda,$$

which is identical with equation (6.36) for the Rayleigh-Jeans radiation law.

Thus the latter is valid for very large values of λT, and the Wien radiation law for small values of λT.

(7) **Einstein's Derivation of Planck's Distribution Laws:** Summarizing the derivation of the radiation law as given in the previous sections, it is seen that the method used consists in treating the hohlraum (black-body enclosure) "as containing modes of electromagnetic vibration of different frequencies and then assigning to each mode of vibration the energy that it should have on the basis of the Maxwell-Boltzmann distribution law as modified to take account of quantum phenomena." [1]

"The above method of derivation gave us, however," as Tolman points out, "no insight into the mechanism by which the continual absorption and emission of radiation by the walls of the container actually does maintain the equilibrium distribution of energy among the different frequencies. In addition the increasingly apparent possibility that radiational energy is actually corpuscular in nature makes the treatment of the hohlraum as a system of modes of electromagnetic vibration seem somewhat artificial. For these reasons, a derivation of the Planck radiation law, by a method which is based on considerations of the probability of the absorption and emission by atoms of radiation of different frequencies, would contain elements of superiority."

This derivation was given by A. Einstein [2] in 1916, and involves the application of two concepts which have been mentioned already. The first of these is Boltzmann's law, which was stated in equation (6.38). The second involves Bohr's postulate that the frequency of any spectral line is determined by the difference in energy values (E_m and E_n) of two discrete stationary states, in accordance with the relation,

$$\nu_{mn} = \frac{E_m - E_n}{h}.\tag{6.49}$$

Let us consider a gas whose molecules are in equilibrium with radiation at a certain temperature. According to classical theory, the energy per molecule can vary continuously from zero to infinity in accordance with the Maxwell-Boltzmann distribution law. However, we must postulate as the fundamental assumption of the quantum theory that such a continuous variation in energy content is impossible. *Each molecule is capable of existing only in a series of discrete states Z_1, Z_2, $\cdots$ Z_m $\cdots$ Z_n, for which the corresponding energies are E_1, E_2, etc.*

Every energy change in such a system including the emission or absorption of radiant energy occurs because of the transition of molecules from one of these states to some other. Bohr, to whom we owe the introduction of this postulate into the quantum theory, has designated Z_1, Z_2, $\cdots$ Z_m, $\cdots$ Z_n as "stationary" states of the system.

---

[1] Tolman, Statistical Mechanics, Chemical Catalog Co., New York (1927), Chap. 16. The passages quoted in this section are taken from the same source.

[2] *Ber. deut. phys. Ges.*, **18**, 318 (1916); also *Physik. Z.*, **18**, 121 (1917).

The relative number of the molecules N_m which are present at any instant in any given state Z_m will be given by the Boltzmann equation.

$$\frac{N_m}{N} = g_m e^{-E_m/kT}, \tag{6.50}$$

where N = number having zero energy, and g_m denotes a constant (known as the *statistical weight*) which is characteristic of the state Z_m and independent of T.*

We shall assume that the energy $E_m - E_n$ is emitted when the molecule passes from state Z_m to state Z_n. Hence the same amount of energy is absorbed when the reverse reaction occurs. (We shall assume $E_m > E_n$). A molecule can pass from state Z_m to Z_n in two ways. First, there may be a spontaneous transition, such as is undergone by radioactive elements.

The rate at which this reaction occurs is given by

$$-\frac{dN_m}{dt} = A_m^n N_m, \tag{6.51}$$

where A_m^n is a constant characteristic of this reaction, and which may be designated as the *probability of spontaneous emission*. It is evident that $1/A_m^n$ corresponds to the "decay period" of the atom Z_m under these conditions where only spontaneous transitions can occur.

Since, however, the molecule is present in an environment which is filled with radiation corresponding to the temperature T, the reaction $Z_m \rightleftarrows Z_n$ is also influenced by this radiation. Let ψ_ν denote the density of the radiation corresponding to frequency ν. We assume that the reaction $Z_m \rightarrow Z_n$ occurs with simultaneous *emission of monochromatic radiation of frequency ν*, and that the reverse reaction occurs with absorption of radiation of the same frequency. The rate of the reaction in either direction depends upon the value of ψ_ν.†

Consequently,

and

$$\left.\begin{aligned} -\frac{dN_m}{dt} &= B_m^n N_m \psi_\nu \\[2mm] -\frac{dN_n}{dt} &= B_n^m N_n \psi_\nu \end{aligned}\right\} . \tag{6.52}$$

Again, the constants B_m^n and B_n^m are of the same nature as the constant A_m^n. The constant B_n^m is designated the *coefficient of absorption* for radiation ν_{mn}, which is defined by equation (6.49).

It is important to realize fully the significance of the assumption involved in equations (6.52). It is assumed that the molecule Z_m or Z_n may be stimulated by radiation of frequency ν *which is characteristic of the reaction $Z_m \rightleftarrows Z_n$,*

---

* In the statement of this law in equation (6.37), g_m was assumed equal to unity, since it is the same for all the harmonic oscillators, independently of the magnitude of the energy.

† ν is used in this and the following equations instead of ν_{mn}.

and while it is relatively easy to understand how the reaction $Z_n \rightarrow Z_m$ can occur by *absorption of energy* from the environment and is therefore governed by the density of the radiation of frequency ν, it is not so evident that the reverse reaction must also depend upon the density of the radiation.

However, it must be remembered that, "on the basis of classical theory, the rate of energy emission of an isolated atom is different from the rate of emission of an atom whose moving electrons are interacting with the varying electromagnetic field present in a radiation field. Hence, to obtain the *total probability of emission* we must include a term depending on the density of radiation."[1] Thus this total probability is given by

$$A_m^n + B_m^n \psi_\nu$$

and B_m^n is designated as the *coefficient of induced emission*.

Now, at equilibrium, the velocities of the two reactions $Z_m \rightleftarrows Z_n$ are equal. Consequently,

$$A_m^n N_m + B_m^n N_m \psi_\nu = B_n^m N_n \psi_\nu. \tag{6.53}$$

Substituting from equation (6.50), it follows that

$$(A_m^n + B_m^n \psi_\nu) g_m e^{-(E_m/kT)} = B_n^m g_n \psi_\nu e^{-(E_n/kT)},$$

that is,

$$A_m^n g_m = \psi_\nu (B_n^m g_n e^{(E_m - E_n)/kT} - B_m^n g_m). \tag{6.54}$$

At infinitely high temperatures the exponential factor obviously tends towards unity. Also ψ_ν increases to infinitely large values at the same time. Since, however, $A_m^n g_m$ is a finite quantity independent of T, it follows that

$$B_n^m g_n = B_m^n g_m \tag{6.55}$$

and, if we denote the ratio A_m^n/B_m^n by α_{mn}, we can replace (6.54) by the equation

$$\psi_\nu = \frac{\alpha_{mn}}{e^{[(E_m - E_n)/kT]} - 1} . \tag{6.56}$$

In order to derive Planck's law from the last equation, it is necessary to compare the latter with the deductions arrived at by Wien and also by Rayleigh and Jeans.

As shown by Wien, it follows from the application of the second law of thermodynamics, that

$$\psi_\nu = \frac{8\pi\nu^3}{c^3} F\left(\frac{\nu}{T}\right) .$$

Hence

$$\alpha_{mn} = \alpha\nu^3$$

and

$$\cdot E_m - E_n = h\nu,$$

where h and α are constants.

[1] Ref. R. C. T., p. 169.

On the other hand, we know that the equipartition law and the Rayleigh-Jeans relation deduced on the basis of this law are valid at very large values of T.

Under these conditions,

$$\psi_\nu = \frac{8\pi\nu^2}{c^3} \, kT.$$ (6.34)

But, from equation (6.56), it is also evident that for extremely high values of T, the quantity $(E_m - E_n)/kT$ is a very small fraction and consequently the equation may be written in the form

$$\psi_\nu = \frac{\alpha\nu^3 kT}{(E_m - E_n)}$$

$$= \frac{\alpha\nu^3 kT}{h\nu} \, .$$ (6.57)

Comparing this equation with (6.34), we obtain the relation

$$\alpha = \frac{8\pi h}{c^3}$$

and hence the final expression for the radiation law may be written in the form

$$\psi_\nu = \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{h\nu/kT} - 1} \, .$$ (6.58)

It will be observed that in Einstein's derivation of the radiation law use is made of Wien's displacement law on the one hand and of the validity, on the other hand, of the Rayleigh-Jeans relation for very long wave lengths. Bose [1] has therefore suggested a derivation of the radiation law which eliminates the support based on classical dynamics involved in these two assumptions.

By making use of the experimentally verified conclusions that the energy of radiation may be treated as constituted of quanta, each having momentum $h\nu/c$, and applying to these quanta the laws of statistical mechanics, he has shown that actually the radiation law may be derived without any appeal whatever to classical dynamics.

While G. N. Lewis [2] has given an extremely interesting derivation of Planck's law by a "kinetic mode of treatment" which does not involve Einstein's theory of induced emission, it should be observed that the experiments of R. Ladenburg [3] and of H. Kopfermann and R. Ladenburg [4] on anomalous dispersion in electrical discharges in neon, apparently require such a theory for a satisfactory interpretation of the results obtained.

[1] *Z. Physik*, **26**, 178 (1924).

[2] *Phys. Rev.*, **35**, 1533 (1930).

[3] *Z. Physik*, **48**, 15 (1928).

[4] *Ibid.*, **48**, 26 (1928); *Z. physik. Chem.*, (Haberband), p. 375 (1928). See discussion of this in Section 16(5).

(8) **Radiation Constants:** Planck's spectral distribution law is usually expressed in the form given in equation (6.46), that is,

$$E_\lambda d\lambda = \frac{c_1 \lambda^5}{e^{c_2/\lambda T} - 1} d\lambda, \tag{6.46}$$

where

$$c_1 = 2\pi c^2 h, \tag{6.47}$$

$$c_2 = ch/k \tag{6.48}$$

and the relation between ψ_ν and E_ν is given by equation (6.3).

Differentiating the right-hand side of (6.46) with respect to λ and equating the resulting expression to zero, we obtain the relation

$$e^x - \frac{xe^x}{5} - 1 = 0, \tag{6.59}$$

where $x = c_2/\lambda_m T$, and λ_m denotes the wave length at which E_λ is a maximum.

The two roots of equation (6.59) are $x = 0$ (which we may disregard) and $x = 4.9651$. Therefore

$$\lambda_m T = \frac{c_2}{4.9651} = A. \tag{6.60}$$

The constant A is known as the Wien Displacement Constant.

The value of E_{λ_m} is given by the relation,

$$E_{\lambda_m} = \frac{2\pi k^5 (4.9651)^5 T^5}{c^3 h^4 (e^{4.9651} - 1)} = BT^5, \tag{6.61}$$

where B is a constant.

Equation (6.60) indicates a method by which c_2 and consequently h/k may be obtained from experimental observations on the value of the constant A.

Since

$$\int_0^\infty E_\lambda d\lambda = E = \sigma T^4$$

it is possible to obtain an expression for the Stefan-Boltzmann constant, σ, by the following procedure: Instead of using the form for Planck's law given in equation (6.46) it is more convenient to express the integral in the form derived from equation (6.44), so that

$$\int_0^\infty E_\nu d\nu = \frac{2\pi h}{c^2} \int_0^\infty \frac{\nu^3 d\nu}{e^{h\nu/kT} - 1}. \tag{6.62}$$

That is,

$$\sigma T^4 = \frac{2\pi k^4 T^4}{c^2 h^3} \int_0^\infty x^3 (e^{-x} + e^{-2x} + e^{-3x} + \cdots) dx, \tag{6.63}$$

where $x = \dfrac{h\nu}{kT}$.

Since

$$\int_0^\infty x^3 e^{-nx} dx = \frac{6}{n^4},$$

and

$$\sum_{n=0}^\infty \frac{1}{n^4} = \frac{\pi^4}{90},$$

we obtain the relation

$$\sigma = \frac{2}{15} \cdot \frac{\pi^5 k^4}{c^2 h^3} \qquad (6.64)*$$

$$= \frac{c_1}{15} \left(\frac{\pi}{c_2} \right)^4. \qquad (6.65)$$

The experimental methods used for the determination of the constants c_2 and σ are described in a number of treatises, especially those dealing with the subjects of heat and pyrometry.[1]

With regard to the accuracy of the considerable number of determinations which have been published since about 1900, H. T. Wensel [2] makes the following comments:

"For practical work, a knowledge of the numerical value of any radiation constant, excepting c_2, to better than 1 or 2 percent, is seldom required. Measurements involving E_λ are usually so made as to depend only on *ratios* in which c_1 cancels out. Even when this is not the case, an accurate value of c_1 is seldom of interest, because we have at present no technique for the accurate measurements of E_λ. The situation in regard to σ is substantially the same. The only experiments in which anything besides an approximate value of σ is of interest are those made for the purpose of determining σ.

"Our interest in the constant c_2 lies in the fact that it is one of the constants used in defining the International Temperature Scale above the melting point of gold. This definition is by means of the formula

$$\ln \left(\frac{E_2}{E_1} \right) = \frac{c_2}{\lambda} \left(\frac{1}{1336} - \frac{1}{T} \right). \qquad (6.66)$$

The constant c_2 is taken as 1.432 cm. degrees. The equation is valid if λT is less than 0.3 cm. degrees. In this equation E_1 and E_2 are the values of E_λ at the melting point of gold, defined as 1336° K, and at the temperature T, respectively. A change in c_2 of 1 per cent results in a change in T of more than 10° at the melting point of platinum and of more than 60° at the melting point of tungsten."

---

* Since $2\pi^4/15 = 12 \times 1.0823$, the latter is often used in the expression for σ.

[1] Ref. H. L., Chapter II. M. N. Saha and B. N. Srivastava, A Text-Book of Heat, Indian Press, Ltd., Allahabad (1931). Measurement of Radiant Energy, W. E. Forsythe, editor, McGraw-Hill Book Company, New York (1937).

[2] *J. Res. Nat. Bur. Stand.*, 22, 375 (1939).

For the "unweighted mean values," Wensel deduces from a summary of the published data, the results:

$$\sigma = 5.69 \times 10^{-5} \text{ erg cm.}^{-2} \text{ sec.}^{-1} \text{ deg.}^{-4},$$
$$c_2 = 1.4364 \text{ cm. deg.,}$$
$$\lambda_m T = 0.2892 \text{ cm. deg.}$$

This value for c_2 is based on optical pyrometer measurements using equation (6.66). On the other hand, the value of c_2 calculated from the observations on $\lambda_m T$ is 1.4361 cm. deg.

F. G. Dunnington [1] concludes from an examination of the data published since 1916 that the most accurate value for σ is $(5.775 \pm 0.022)10^{-5}$ c.g.s. units, and for c_2 he accepts the value 1.432 ± 0.003 cm. deg., which was used by R. T. Birge in his 1929 publication.

On the whole it is probably better, as Wensel has suggested, to calculate the values for the radiation constants from the atomic constants h and e. Table 6.2 gives two sets of values calculated (a) on the basis of values recommended by Birge, that is, $e = 4.8022 \times 10^{-10}$ e.s.u., $h = 6.6236 \times 10^{-27}$ erg sec.; (b) on the basis, of values recommended by Wensel, that is, $e = 4.800 \times 10^{-10}$ e.s.u.; $h = 6.61 \times 10^{-27}$ erg sec.

<div align="center">TABLE 6.2 *</div>

Dimensions		Birge	Wensel
$10^{16} k$ . . . . .erg deg.$^{-1}$		1.3805.	1.380
$10^5 c_1$ . . . . .erg cm^2 sec.$^{-1}$		3.740	3.732
c_2 . . . . .cm. deg.		1.4383.	1.436
A . . . . .cm. deg.		0.2897.	0.2892
$10^{11} B$ . . . . .watt cm.$^{-3}$ deg.$^{-5}$		1.2881.	1.2965
$10^{12} \sigma$ . . . . .watt cm.$^{-2}$ deg.$^{-4}$		5.6751	5.70
$10^{15} a$ . . . . .erg cm.$^{-3}$ deg.$^{-4}$		7.572	7.605

* Note: $A = \lambda_m T$; $B = E_{\lambda_m} \cdot T^{-5}$; $a = 4\sigma/c$; 10^7 erg sec.$^{-1}$ = 1 watt.

Fig. 6.2 shows plots of the energy distribution function according to Planck, for three different temperatures, calculated on the basis of the radiation constants deduced by Birge. For $T = 5000°$ K, the maximum value of E_λ derived from equation (6.61) is 4.027×10^7 watts cm^{-3}. Hence 1 unit on the ordinate scale = 4.027×10^6 watts cm^{-3}. The arrows indicate the values of λ_m for each value of T. The area under each curve gives the value of

$$E = \int_0^\infty E_\lambda d\lambda = \sigma T^4 \qquad (6.67)$$

in watts. cm^{-2}. Hence, the mean value of λ, defined by the relation

$$E_m \cdot \bar{\lambda} = \sigma T^4 = 3$$

[1] Rev. Mod. Phys., 11, 65 (1939).

is 0.881×10^{-4} cm. for $T = 5000°$ K (on the basis of the value $E = 3548$ watts cm.$^{-2}$, given in Table 6.2).*

It is of interest to compare these values of E_λ for $T = 5000°$ K, with those deduced from the Rayleigh-Jeans equation (6.36) and those deduced from the Wien equation (6.19).

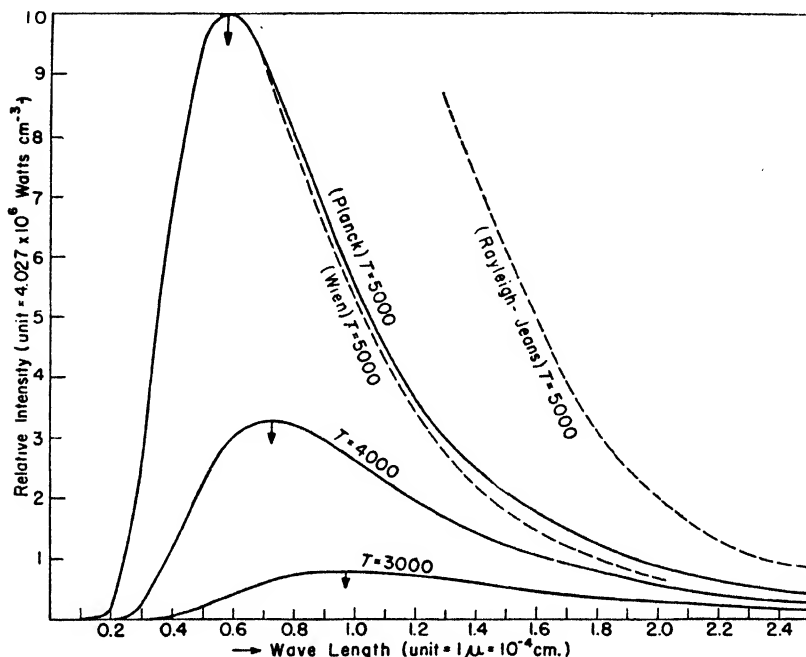FIG. 6.2.   Plots of Energy Distribution for a Black-Body Radiator According to Equations of Planck (for $T = 3000$, 4000 and 5000° K) and Those of Wien and Rayleigh-Jeans (for $T = 5000°$ K).

Let $(E_\lambda)_P$ denote the value derived for given values of λ and T on the basis of Planck's relation, and let $(E_\lambda)_W$ and $(E_\lambda)_R$ designate the values derived for the same values of λ and T by means of the Wien and Rayleigh-Jeans equations respectively.   It is readily deduced from these equations that the

* It is of interest in this connection to mention the publication by A. N. Lowan and G. Blanck (*J. Opt. Soc. Am.*, **30**, 70 (1940) of tables of

$$E_\lambda; \quad N_\lambda = E_\lambda/h\nu; \quad \int_0^\infty E_\lambda d\lambda, \quad \text{and} \quad \int_0^\infty N_\lambda d\lambda,$$

as functions of λ and T.   The quantity N_λ corresponds to the number of photons emitted in the wave length range from λ to $\lambda + d\lambda$, per unit time, per unit area, throughout the solid angle 2π steradians.

following relations are valid:

$$\frac{(E_\lambda)_W}{(E_\lambda)_P} = \frac{e^{c_2/\lambda T} - 1}{e^{c_2/\lambda T}},$$ (6.68)

$$\frac{(E_\lambda)_R}{(E_\lambda)_P} = \frac{\lambda T}{c_2}(e^{c_2/\lambda T} - 1).$$ (6.69)

Using the value $c_2 = 1.4383$ cm. deg., the values of the ratios deduced for $T = 5000°$ K, are those given in Table 6.3. The values of E_λ for this temperature as deduced by the Rayleigh-Jeans and Wien equations are shown by the dotted curves in Fig. 6.2. It will be observed from Table 6.3 that while the Wien equation gives satisfactory results in the visible and ultraviolet region (that is, for $\lambda < 0.7 \times 10^{-4}$ cm.), the Rayleigh-Jeans equation yields even approximately satisfactory agreement with the Planck equation only for extremely long wave lengths (in the far infra-red).

TABLE 6.3

$10^4\lambda$(cm.)	$(E_\lambda)_W/(E_\lambda)_P$	$(E_\lambda)_R/(E_\lambda)_P$
∞	0.	1.
10.0	0.249	1.154
5.0	.447	1.341
2.5	.683	1.875
2.0	.762	2.220
1.8	.800	2.468
1.6	.835	2.802
1.4	.872	3.311
1.0	.944	5.825
0.6	.991	—
0.0	1.000	∞

7. MATTER WAVES

(1) **The de Broglie Wave Length:** In the previous sections different effects have been described which lead to a corpuscular theory of radiant energy. We find that radiation exhibits, on the one hand, a behavior associated with wave motion, such as diffraction, interference, and polarization phenomena, and on the other, characteristics which can be ascribed only to light particles or photons. It is a rather remarkable coincidence in the history of physics that just at the moment when the explanation for the observed dualism in the nature of radiation seemed quite remote, a solution developed as a result of the discovery that corpuscles in motion also exhibit phenomena which can be interpreted only on the basis of a wave theory.

That such phenomena might be expected were first suggested by some speculations of L. de Broglie in 1924.[1] It is a well known fact that the laws

[1] *Phil. Mag.*, **47**, 446 (1924); *Ann. physique*, **3**, 22 (1925); *J. phys. rad.*, [7], **1**, 321 (1926). Translations of the last two papers are contained in the book, "Selected Papers on Wave Mechanics," by L. de Broglie and L. Brillouin, Blackie and Son, Ltd., London and Glasgow, 1928.

of geometrical optics are valid so long as the wave length, λ, is small compared with the radius of curvature, r, of the path of the rays. For a value of r of the same order of magnitude as, or less than, λ, the problem of the propagation of light must be treated as a wave motion. Is it not possible, de Broglie asks, that for the motion of electrons in atoms, the application of the laws of ordinary mechanics is limited by similar considerations?

According to the simple Bohr theory of the hydrogen atom, the electron may revolve in any one of the discrete circular orbits defined by the quantum condition that the angular momentum is an integral multiple of h, that is,

$$2\pi mvr = nh, \tag{7.1}$$

where v is the velocity of the electron in an orbit of radius r, and $n = 1, 2, \cdots$.

Now let us introduce the assumption that with this motion is associated a "wave length" λ, such that

$$n\lambda = 2\pi r. \tag{7.2}$$

(To assume that the circumference is not equal to an integral number of wave lengths would be physically inconceivable.) Then, it follows from these two equations that

$$\lambda = \frac{h}{mv} = \frac{h}{p}, \tag{7.3}$$

where p = momentum of electron in its orbit, and λ is designated the de Broglie wave length.

Why should the possible observation of such a phenomenon be limited to atomic dimensions? A simple calculation shows the reason. For a mass of 10^{-6} gm. moving with a velocity of 10^{-4} cm. sec.$^{-1}$, $p = 10^{-10}$ and hence $\lambda = 6.6 \times 10^{-17}$, a magnitude which is approximately 10^{-9} of that associated with atomic diameters. On the other hand, in the case of an electron moving with a velocity of 5.9×10^7 cm. sec.$^{-1}$, (corresponding to 1 electron volt), the magnitude of p is approximately 5.5×10^{-20} c.g.s. unit, and consequently $\lambda = 12 \times 10^{-8}$,—a magnitude which could be measured by means of a crystal grating. That such wave lengths have been found associated with the motion of electrons is shown in the following section.

The striking point about de Broglie's hypothesis is that it suggested a dualism in the behavior of matter which is analogous to that already described in connection with the phenomena of interaction between energy and matter. This analogy is most readily evident when we consider that in the case of photons, the momentum is determined by the relation, used in discussing the Compton effect,

$$p = \frac{h\nu}{c} = \frac{h}{\lambda}, \tag{7.4}$$

which is identical with de Broglie's relation.

(2) **Experiments on Electron Reflection and Diffraction:** Shortly after the appearance of de Broglie's first publications W. Elsasser [1] predicted the possibility that in the interaction between electrons and a crystal, the former would exhibit the characteristics of wave motion. Experimental evidence of this nature was soon forthcoming as a result of two series of investigations, one by C. Davisson and L. H. Germer [2] and the other by G. P. Thomson and A. Reid.[3]

The arrangement used by Davisson and Germer is indicated in Fig. 7.1. The electrons emitted from a tungsten cathode are accelerated through a
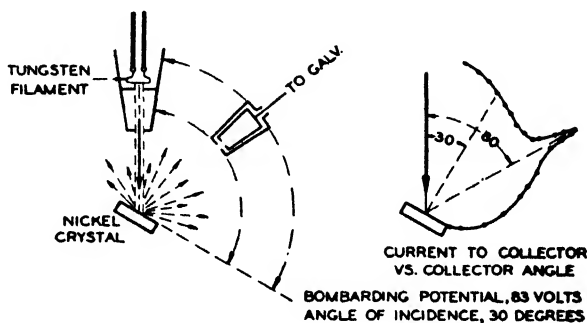
Fig. 7.1. Schematic Representation of Arrangement for Measuring Effect of Angle of Incidence on Intensity of Reflected Electron Beams

definite potential applied to the shielding box and then fall on one of the surfaces of a single crystal of nickel. The electrons reflected from the nickel surface at different angles are detected by the galvanometer connected with the Faraday cage. The right-hand figure shows the variation in intensity of reflected electron current as the collector is moved along the arc indicated in the left-hand figure. It will be observed that the maximum intensity of collector current is obtained when the angle of reflection is equal to the angle of incidence.

"There is no doubt," as Germer points out,[4] "that the incident electrons recognize the surface of the crystal, and prefer to move off in the direction of regular reflection. And this does not occur except when the surface is a definite crystallographic plane." There are no reflections from a polycrystalline surface.

It is observed also, that for a given angle of incidence the intensity of the regularly reflected beam passes through successive maxima and minima with

[1] *Naturwiss.*, **13**, 711 (1925).

[2] *Phys. Rev.*, **30**, 705 (1927); *Bell Tech. J.*, **7**, 1 (1928); *J. Franklin Inst.*, **205**, 597 (1928); *Proc. Nat. Acad. Sci.*, **14**, 317, 619 (1928); L. H. Germer, *J. Chem. Ed.*, **5**, 1041, 1255 (1928); C. J. Davisson, *J. Opt. Soc. Am.*, **18**, 193 (1929); see also ref. F. K. R., Chapter 15.

[3] *Proc. Roy. Soc.*, [A], **117**, 600 (1928); **119**, 651 (1928). This work as well as that of Davisson and Germer is discussed also by G. P. Thomson, The Wave Mechanics of Free Electrons, McGraw-Hill Book Co. (1930).

[4] *J. Chem. Ed.*, **5**, 1041 (1928).

increase in speed, as shown in **Fig. 7.2**. The abscissae in this plot give the velocity, v, in accordance with the equation

$$v = \sqrt{2Ve/m}. \tag{7.4}$$

These results are quite similar to those observed in the selective reflection of X-rays. According to Bragg's theory, the intensity of a reflected beam is
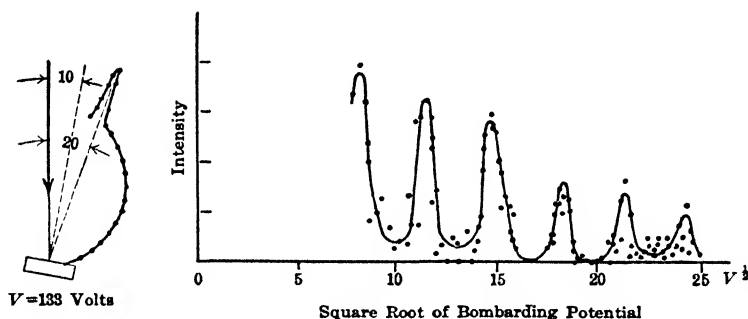

$V = 133$ Volts

Square Root of Bombarding Potential

FIG. 7.2. Relation Between Intensity of Reflected Electron Beam and Bombarding Potential

a maximum when

$$2d \cos \theta = n\lambda, \tag{7.5}$$

where d = distance between layers of atoms *parallel* to the surface,

θ = angle of incidence = angle of reflection, and

n is an integer.

That is, the intensity of the reflected beam is a maximum for values of λ given by the relation,

$$\frac{1}{\lambda} = \frac{n}{2d \cos \theta} . \tag{7.6}$$

Therefore, a plot of intensity versus $1/\lambda$ for a given value of θ should show maxima at equal intervals given by $1/(2d \cos \theta)$. If de Broglie's hypothesis is valid, then the value of λ obtained by application of this equation should be in agreement with equation (7.3) which may be expressed in the form

$$\lambda = \sqrt{\frac{h^2}{2me} \cdot \frac{300}{V}} = \frac{12.26}{\sqrt{V}} \text{ Å} = \sqrt{\frac{150.04}{V}} \text{ Å} \tag{7.7}$$

where V is expressed in volts, λ, in Ångström units, and the values used for h, e, and m are those adopted in this chapter.

In Davisson and Germer's experiments, it was observed that for relatively high velocities of electrons ($\lambda = 0.5$ Å) the agreement between equations (7.6) and (7.7) is good, but for lower speeds (smaller values of $1/\lambda$) the actual maxima

do not fall at exactly equal intervals and the agreement between values of λ calculated by means of the two equations is only approximate. This discrepancy, it was found, could be accounted for by assuming for the de Broglie waves a refractive index greater than unity.[1]

While the results just described were obtained with beams for which the angle of incidence with respect to the normal varied from 10° to 50°, a series of experiments were carried out in which the electrons were made to strike the surface at *normal* incidence.

From X-ray measurements it is known that a nickel crystal is of the face-centered cubic type, as shown in Fig. 7.3.[2] In preparing the crystal for bom-
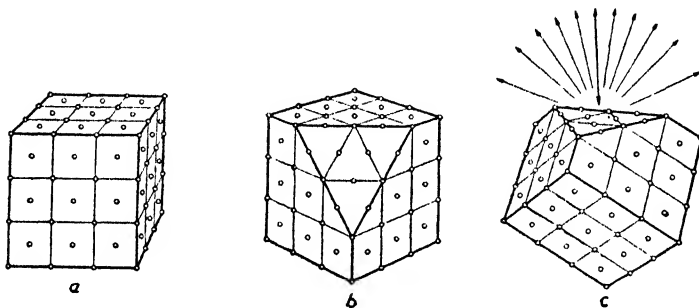

FIG. 7.3. Arrangement of Atoms in Nickel Lattice, in Cut Lattice, and Directions of Incident and Scattered Electron Beams

bardment a cut was made through the cube structure at right angles to one of the cube diagonals, as shown in Fig. 7.3b. The directions of the incident and scattered electron beams are indicated in Fig. 7.3c. The procedure used in carrying out the observation is described by Davisson as follows:

"We are to think of electrons raining down normally upon the triangular surface, and of some of these emerging from the crystal without loss of energy, and proceeding from it in various directions. What is measured is the current density of these full speed scattered electrons as a function of direction and of bombarding potential. The way in which the measurements are made is illustrated in Fig. 7.4. The electrons proceeding in a given direction from the crystal enter the inner box of a double Faraday collector and a galvanometer of high sensitivity is used to measure the current to which they give rise. An appropriate retarding potential between the parts of the collector excludes from the inner box all but full speed electrons.

"The collector may be moved over an arc of a circle in the plane of the drawing as indicated, and the crystal may be rotated about an axis which coincides with the axis of the incident beam of electrons. Thus the collector may be set for measuring the intensity of scattering in any direction relative to the crystal—by turning the crystal to the desired azimuth, and moving the collector to the desired colatitude. The whole solid angle in front of the crystal may be thus explored with the exception of the region within twenty degrees of the incident beam.

"Certain of the azimuths related most simply to the crystal structure we shall refer to as 'principal azimuths.' Thus there are the three azimuths that include the apexes of the

[1] L. H. Germer, *J. Chem. Ed.*, 5, 1255 (1928).

[2] C. J. Davisson, *Bell Tech. J.*, 7, 90–105 (1928).

triangle. If we find the intensity of scattering depending on colatitude in a certain way in one of these azimuths, we expect, of course, to find it depending upon colatitude in the same way in each of the other two. We shall call these the '*A*-azimuths.' On the left in Fig. 7.4 the crystal has been turned to bring one of the *A*-azimuths into the plane of rotation of the collector.

"Another triad of principal azimuths consists of the three which include the mid-points of the sides of the triangle. These we shall call the '*B*-azimuths.' The next most important family of azimuths comprises those which are parallel to the sides of the triangle; of these there are six, the '*C*-azimuths.'

"If we turn the crystal to any arbitrarily chosen azimuth, set the bombarding potential at any arbitrarily chosen value, and measure the intensity of scattering as a function of colatitude, what we find ordinarily is the type of relation represented by the curve on the left in Fig. 7.5.
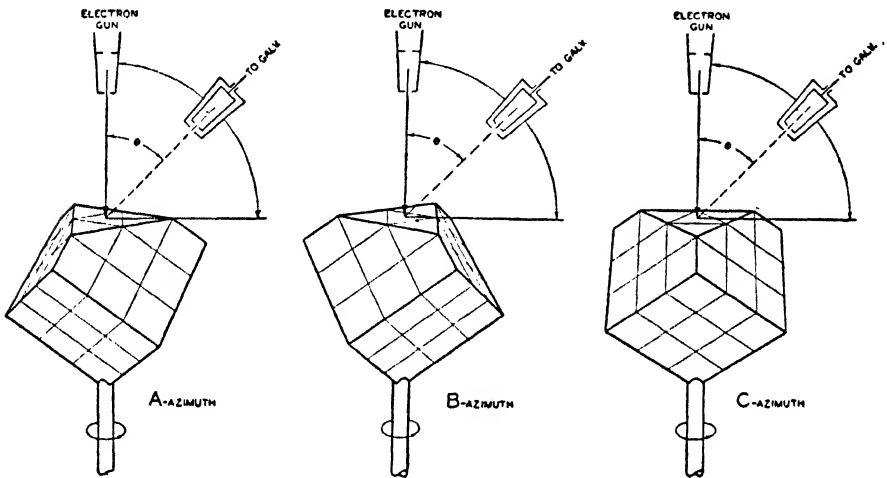

FIG. 7.4. Showing the Three Principal Azimuths

"This curve is actually one found for scattering in the *A*-azimuth when the bombarding potential is 36 volts. It is typical, however, of the curves that are obtained when no diffraction beam is showing. The intensity of scattering in a given direction is indicated by the length of the vector from the point of bombardment to the curve. The intensity is zero in the plane of the crystal surface, and increases regularly as the colatitude angle is decreased. This type of scattering forms a background upon which the diffraction beams are superposed.

"The occurrence of a diffraction beam is illustrated in the series of curves to the right in Fig. 7.5. When the bombarding potential is increased from 36 to 40 volts, the curve is characterized by a slight hump at colatitude 60 degrees. With further increase in bombarding potential this hump moves upward, and at the same time develops into a strong spur. The spur reaches its maximum development at 54 volts in colatitude 50 degrees, then decreases in intensity, and finally vanishes from the curve at about 70 volts in colatitude 40 degrees.

"We next make an exploration in azimuth through this spur at its maximum; we adjust the bombarding potential to 54 volts, set the collector in colatitude 50 degrees, and make measurements of the intensity of scattering as the crystal is rotated. The results of this exploration are exhibited by the curve at the bottom of Fig. 7.5, in which current to the collector is plotted against azimuth. We find that the spur is sharp in azimuth as well as in latitude and that it is one of a set of three spurs as required by the symmetry of the crystal."

Similar observations made in the *B*-azimuth showed a maximum intensity of the scattered electrons at 44 degrees and 65 volts.

"Let us try now," Davisson continues, "to forget that what we are measuring in these experiments is a current of discrete electrons arriving one by one at our collector. Let us imagine that what we are dealing with is indeed a monochromatic wave radiation, and that our Faraday box and galvanometer are instruments suitable for measuring the intensity of this radiation. We are to think of the incident electron beam as a beam of monochromatic waves, and of the '54-volt beam' in the *A*-azimuth and the '65-volt beam' in the *B*-azimuth as diffraction beams that owe their intensities, in the usual way, to constructive interference among elements of the incident beam scattered by the atoms of the crystal. With this picture in mind we try next to calculate wave lengths of this electron radiation from the data of these beams and from the geometry and scale of the crystal.
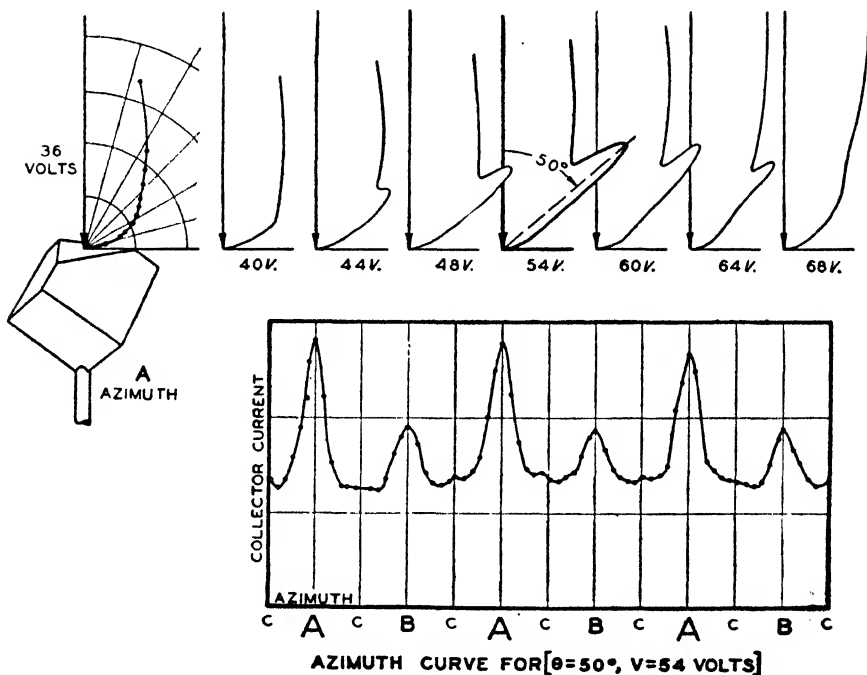

Fɪɢ. 7.5.   Curves Showing Development of Diffraction Beam in the *A*-Azimuth

"To begin with, we shall need to look more closely into our crystal. The atoms in the triangular face of the crystal may be regarded as arranged in lines or files at right angles to the plane of the *A*- and *B*-azimuths. If a beam of radiation were scattered by this single layer of atoms, these lines of atoms would function as the lines of an ordinary line grating. In particular, if the beam met the plane of atoms at normal incidence, diffraction beams would appear in the *A*- and *B*-azimuths, and the wave lengths and inclinations of these beams would be related to one another and to the grating constant *d* by the well-known formula, $n\lambda = d \sin \theta$,[*] as illustrated at the top of Fig. 7.6."

[*] In this relation θ is the *glancing* angle, and $(\pi/2) - \theta$ is the angle of incidence.

Applying this simple formula to the 54-volt and 65-volt beams, we find for the former the value $n\lambda = 2.15 \times \sin 50° = 1.65$ Å, and for the latter the value $n\lambda = 1.50$ Å. On the other hand, we find from equation (7.7) for λ, the values 1.67 Å and 1.52 Å respectively.

As Davisson points out: "In the actual experiments the diffracting system is not quite so simple. It comprises not a single layer of atoms, but many layers; it is equivalent not to a single line grating, but to many line gratings piled one above the other, as shown graphically at the bottom of the figure." However, it is not necessary in this connection to discuss this complication at greater length.* The essential point is that a large number of observations
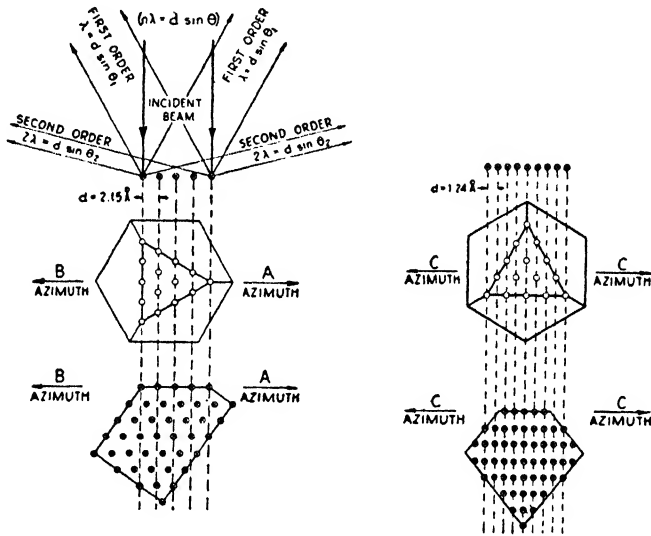

Fɪɢ. 7.6.   Illustrating $n\lambda = d \sin \theta$ Relation in the Three Azimuths

were made with electron beams up to 370 volts, and in all cases the results were found to be in agreement with de Broglie's relation, within the limits of experimental error.

(3) **Transmission of Electrons through Thin Films**: In the classic experiments of Friedrich, Knipping and Laue a beam of X-rays was transmitted through a crystal on to a photographic plate and the resulting pattern of spots was interpreted as indisputable evidence for the wave nature of these radiations. If electrons also behave as waves then it should be possible to obtain diffraction patterns similar to those observed with X-rays, by transmission of electrons through crystals. Because of the much greater absorption of electrons by crystals, G. P. Thomson and A. Reid used thin metal foils. When

* See ref. F. K. R. for further remarks.

examined by means of transmitted X-rays the observed diffraction patterns consist of concentric rings instead of the spots observed in the Laue patterns. This is due to the fact that thin metal foil actually behaves as an aggregate of very small crystals oriented in random directions. When cathode rays were transmitted through such foils of aluminum and gold to a photographic plate, rings were obtained similar to those obtained by the Hull-Debye-Scherrer method used for obtaining the crystal structure of materials in powder form.

From measurements of the diameters of the rings and a knowledge of the crystal grating space it is possible to determine the wave length of the incident radiation. If L is the distance of the plate from the scattering substance, D the diameter of the ring produced by diffraction of that set of planes for which d is the distance of separation, then:

$$\frac{2n\lambda}{d} = \frac{D}{L}, \tag{7.8}$$

where n is the order of the ring.

For electrons accelerated by higher voltages, such that the ratio β of the velocity to that of light is appreciable, the de Broglie relation assumes the form: [1]

$$\lambda = \sqrt{\frac{h^2}{2m_0e} \cdot \frac{300}{V}} \left(1 - \frac{\alpha}{4} + \frac{3\alpha^2}{32} \right), \tag{7.9}$$

where

$$\alpha = \frac{eV}{300 \, m_0c^2} \approx 2 \times 10^{-6} V$$

and V is expressed in ordinary volts.

It will be observed that the first term on the right-hand side of equation (7.9) is identical with equation (7.7), and the correction terms involving α amount to about 2.5 per cent for 50,000 volt electrons and to about 8.5 per cent for 200,000 volt electrons.

Taking into account only the term $\alpha/4$, equation (7.9) can be written in the form

$$\lambda\sqrt{V} \left(1 + \frac{\alpha}{4} \right) = h \sqrt{\frac{150}{m_0e}}. \tag{7.10}$$

In consequence of equation (7.8) it follows that for a given set up of the experiment, $D\sqrt{V}(1 + \alpha/4)$ should be a constant. Table 7.1 gives the results obtained by G. P. Thomson [2] for two metal films.

Table 7.2 [3] gives the values of a, the size of the unit cube, calculated for several metal foils from electron diffraction measurements, and for comparison the values obtained by means of X-ray diffraction observations.

[1] Ref. F. K. R., p. 677.
[2] Wave Mechanics of Free Electrons, p. 63.
[3] *Op. cit.*, p. 69.

TABLE 7.1

Aluminum			Gold		
V	D cm.	$D\sqrt{V}(1 + \alpha/4)$	V	D cm.	$D\sqrt{V}(1 + \alpha/4)$
17,500	3.1	415	24,600	2.50	398
30,500	2.45	434	31,800	2.15	390
31,800	2.32	418	39,400	2.00	404
40,000	2.12	430	45,600	1.86	405
44,000	2.08	445	54,300	1.63	388
48,600	1.90	430	61,200	1.61	410
48,600	1.98	446		Mean	399
56,500	1.83	446			
56,500	1.80	438			
	Mean	434			

TABLE 7.2

Size of Unit Cube, a (Ångströms)

Metal	X-ray Method	Electron Diffraction	
Aluminum	4.046	4.06;	4.00
Gold	4.06	4.18;	3.99
Platinum	3.91	3.88;	3.89
Lead	4.92	4.99	
Iron	2.87	2.85	
Silver	4.079	4.11	
Copper	3.60	3.66	

"The agreement is thus entirely satisfactory," as Thomson points out, "and we are driven to suppose that the electrons form diffraction patterns just similar to those which would be produced by waves of $\lambda = h/mv$. All we had to assume, in deducing these results, is that each atom acts as a scattering center and that the scattered waves are coherent in phase and wave length with the incident train."

E. Rupp [1] carried out similar measurements with slow electrons of 150–290 volts energy, using extremely thin metal films, (thickness about 10^{-6} cm.) and obtained good agreement with de Broglie's relation.

Using very thin films of mica, S. Kikuchi [2] has obtained diffraction patterns similar to those observed for single crystals by Friedrich, Knipping and Laue with X-rays. The lattice constants calculated from the position of the various spots were found to be in excellent agreement with those deduced by use of X-ray diffraction patterns. In these experiments Kikuchi worked with electron energies up to 78,000 volts.

[1] *Ann. Physik*, 85, 981 (1928); 1, 773 (1929).
[2] *Jap. J. Phys.*, 5, 83 (1928), also described by G. P. Thomson, *op. cit.* and ref. F. K. R.

(4) **Applications of Electron Diffraction Studies:** [1] Since Debye had shown previously that the positions of atoms in molecules could be determined from measurements on the scattering of X-rays by gases and vapors, it followed naturally that experiments of a similar nature should be undertaken with electron beams. Among the first investigators in this field were H. Mark and R. Wierl.[2] Using electrons of 43,000 volt energy, corresponding to a de Broglie wave length of 0.0578 Å, they determined atomic arrangements and interatomic distances in a number of gases and vapors such as CO_2, Br_2, CCl_4, $SiCl_4$, C_6H_6, and C_6H_{14}.

During the intervening period this method of investigating molecular structures has also been applied extensively by a number of workers both in this country and abroad. A review of the results obtained has been published by L. O. Brockway[3] which demonstrates the great utility of this new tool for attacking problems of interest to the chemists.

In the original papers of Davisson and Germer, there were discussed some observations made with gas films adsorbed on the nickel surfaces. Since then L. H. Germer has applied the electron diffraction method to the study of different types of surface films, including those obtained from monomolecular layers of barium stearate and similar compounds on water (Langmuir films).[4] "The low penetrating power of electrons as compared with X-rays makes the former *particularly* adapted to the study of surface characteristics." [5]

For the investigation of the atomic arrangement in solids, it is necessary to use electron beams in the range of 30 to 50 kilovolts and very thin films of the order of 10^{-5} to 10^{-4} cm. Some of the first experiments were carried out by G. P. Thomson with thin films of celluloid. In the case of metals such as gold, platinum and copper films were obtained by chemical etching of beaten foil. F. Kirchner[6] has improved this technique by preparing extremely thin films of collodion (which absorb the electrons to only a small extent) upon which films of metal or even inorganic compounds are deposited by evaporation in a vacuum.[7]

(5) **Application of de Broglie's Relation to Accurate Determination of Physical Constants:** From accurate determinations of λ and V, it is evidently possible, by means of electron diffraction measurements to deduce precision values of the ratio $h/\sqrt{me}$. Again, it follows from the relation $h/\lambda = mv$ that, from exact measurements of λ and of the speed of the electrons, it is possible

---

[1] A comprehensive review of this subject has been published by J. T. Randall, The Diffraction of X-rays and Electrons by Amorphous Solids, Liquids, and Gases, John Wiley and Sons, New York (1934).

[2] H. Mark and R. Wierl, *Naturwiss.*, **18**, 205 (1930); *Z. Physik*, **60**, 741 (1931). R. Wierl, *Ann. Physik*, **8**, 521 (1931); **13**, 453 (1933).

[3] *Rev. Mod. Phys.*, **8**, 231 (1936).

[4] L. H. Germer, *J. Chem. Ed.*, **5**, 1255 (1928).

[5] L. O. Brockway, *loc. cit.*

[6] *Ann. Physik*, **11**, 741 (1931).

[7] *Trans. Faraday Soc.*, **31**, 1043 (1935) contains a report of a symposium on diffraction by solids.

to derive the value of the ratio h/m. Mention has already been made of the fact that, in their experiments, Davisson and Germer as well as G. P. Thomson obtained very close quantitative agreement between the observed values of λ and those calculated on the basis of generally accepted values of h, m, and e. In the present section we shall discuss briefly the results of more recent work aimed at precision measurements of these three constants.

One of the important problems in such investigations is the determination of the velocity of the electrons. Instead of deriving this from a measurement of the accelerating voltage, J. Gnan,[1] has measured the electron velocities in terms of a distance and an electrical frequency. The electrons were transmitted through a thin film of bismuth (for which the lattice constants are known), and the wave length determined by applying the Bragg relation,

$$2d \sin \theta = n\lambda.$$

The average value obtained was $h/m_0 = 7.252$ c.g.s. units,[2] as compared with the value 7.273 recommended by Birge.

However, the value of d deduced by X-ray methods depends upon the value of e in equations (3.4) and (3.5) which may be expressed in the form

$$N = \frac{M}{2d^3\phi\rho} = \frac{Fc}{e}.$$

Hence,

$$h/m_0 \sim e^{1/3},$$

and consequently a change in the assumed value of e from 4.774 to 4.803 leads to an increase of approximately 0.2 per cent in the value of h/m_0, which would bring the value 7.252 up to 7.267.

The method used by S. von Friesen is described by him as follows:[3] "The wave length was measured for electrons of known velocity. The voltage accelerating the electrons was obtained from a high-voltage source by utilizing the Greinacher principle. A separate electron-valve device stabilized the voltage which remained constant within a few hundredths of a per cent. The voltage was measured against a standard cell by means of a wire-wound potentiometer. The wave lengths were obtained from spectra produced by diffraction with etched galena crystals. A beam of electrons defined by two narrow slits fell on the crystal, at grazing incidence, and penetrated small lumps of galena projecting from the surface. The lumps had retained their original orientation to the large crystal and acted as a transmission grating. They gave rise to vary sharp spectral lines which could be photographed and measured with high accuracy."

[1] *Ann. Physik*, **20**, 361 (1934).

[2] Based on the value of d obtained by Jette and Foot, *Phys. Rev.*, **39** 1018 (1932); also, *ibid.*, **58**, 81 (1940).

[3] *Proc. Roy. Soc.*, [**A**], **160**, 424 (1937). The original work was published in an "Inaugural Dissertation," Upsala (1936).

What was actually measured in these experiments was the value of $h/\sqrt{m_0 e}$, or $(h/e)(e/m_0)^{1/2}$. A recalculation of von Friesen's data yields, according to F. G. Dunnington,[1] a value for this constant of $(1.00084 \pm 0.00058) \times 10^{-8}$ e.s.u. Assuming the value $(e/m_0)c = 5.273 \times 10^{17}$, this corresponds to the value $h/e = 1.378 \times 10^{-17}$ erg sec. e.s. unit^{-1}.

(6) **Summary of Methods for the Evaluation of the Constants h, m, and e:** In the previous sections a number of methods have been described for the evaluation of the constant h. These methods also involve determinations of one or both of the constants e and m, as well as other constants such as F, the Faraday constant, c, the velocity of light, k_λ, the ratio between the grating unit of X-ray wave length and the Siegbahn unit,* and R, the gas constant.

As mentioned already the results obtained have been subjected to detailed critical analysis by F. G. Dunnington,[2] H. T. Wensel,[3] J. W. M. DuMond,[4] and F. Kirchner.[5] More recently C. G. Darwin [6] and DuMond [7] have also published critical discussions of the same topic.

Table 7.3 which is based on similar tables by Dunnington and Darwin and represents a condensation of a much more elaborate table by DuMond,[6] gives

TABLE 7.3

No.	Experiment	Constant	Dunnington	Birge	Other Constants
1.	Ruled grating	$10^{10}e$	4.8025	4.8022	$Fqck\lambda^3$
2.	Oil drop	$10^{10}e$	4.8036		cr^{-1}
3.	Limit of continuous X-rays	$10^{17}h/e$	1.3763	1.3793	$rc^{-2}k_\lambda$
4.	Ionization and excitation	$10^{17}h/e$	1.3745		rc^{-2}
5.	Radiation (c_2)	$10^{17}h/e$	1.3730		$Rc^{-2}F^{-1}q^{-1}$
6.	Stefan	$10^{-10}e/h^{3/4}$	2.0778	2.0683	$Fqc^{3/2}R^{-1}$
7.	Electron diffraction	$10^8 \left(\dfrac{h}{e}\right)\left(\dfrac{e}{m_0}\right)^{1/2}$	1.00084	1.0016	$r^{1/2}c^{-1/2}k_\lambda$
8.	Electron diffraction	h/m_0	7.274	7.273	k_λ
9.	Compton effect	h/m_0	7.264		$k_\lambda c$
10.	Specific charge	$10^{-7}e/m_0$	1.7591	1.7591	Various
11.	X-ray photoelectrons	$10^{-34}\left(\dfrac{e}{m_0}\right)\left(\dfrac{e}{h}\right)$	3.8220	3.8232	$c^2p^2k_\lambda^{-1}r^{-2}$
12.	Rydberg number	$10^{-14}e^4m_0/h^3$	1.666564	1.66656	c

p = Ratio of int. ohm to abs. ohm,
q = " " " ampere to abs. ampere,
r = " " " volt to abs. volt.

[1] *Rev. Mod. Phys.*, 11, 65 (1939).
* See discussion at the end of Section 3(1), p. 162.
[2] *Rev. Mod. Phys.*, 11, 65 (1939).
[3] *J. Res. Nat. Bur. Stand.*, 22, 375 (1939).
[4] *Phys. Rev.*, 56, 153 (1939).
[5] *Ergebn. exakt. Naturwiss.*, 18, 26 (1939).
[6] *Proc. Phys. Soc.* (London), 52, 202 (1940).
[7] *Phys. Rev.*, 58, 457 (1940). This paper contains a very comprehensive survey of values obtained in the different investigations.

a summary of the different types of experiments and the results obtained. The fourth column gives the most probable value according to Dunnington and the next column gives for comparison the value suggested by Birge. The last column gives the other constants involved in these determinations, which have been defined above, while the significance of the other three constants, p, q, and r, is given at the bottom of the table.

The most noteworthy feature about the results shown in this table is the fact that the direct methods for the determination of h/e lead to values which are consistently lower than that based on e, e/m_0, and R_∞, which has been advocated by Birge.* The existence of this discrepancy has been emphasized by Dunnington, Darwin and DuMond, and its occurrence may be of fundamental significance, but it presents a problem which can be solved only by further careful experimental work.

8. Corpuscles and Waves †

(1) **Dualistic Interpretation of Refraction:** In the previous sections observations have been described which indicate that both electrons and radiations exhibit properties associated on the one hand, with corpuscular motion and on the other, with wave motion. How may these observations be interpreted? The dilemma reminds us of the alternative methods proposed by Newton and Huyghens for the mechanism of the propagation of light.

Let us consider the refraction of light at a surface separating two media, 1 and 2. If θ_1 denotes the angle between the direction of the incident beam of light and the normal to the surface, and θ_2 denotes the corresponding angle for the refracted ray, then, on the basis of the undulatory theory,

$$\frac{u_1}{u_2} = \frac{\sin \theta_1}{\sin \theta_2} = n_{12}, \tag{8.1}$$

, where u_1 and u_2 designate the velocity of the wave front in each of the two media and n_{12} is a constant, known as the refractive index.

From the point of view of corpuscular motion, the refraction is due to a change in the component of momentum normal to the surface of separation. Let p_1^n and p_1^t denote the normal and tangential components, respectively, of the momentum in medium 1 (see Fig. 8.1), and p_2^n and p_2^t the corresponding components in medium 2. In the process of refraction only the normal component changes. Hence:

$$p_1^t = p_2^t$$

---

* A new determination of the value of R_∞ by J. W. Drinkwater, O. W. Richardson, and W. E. Williams, *Proc. Roy. Soc.*, [A], **174**, 164 (1940) leads to the result $R_\infty = 109{,}737.26 \pm 0.020$ cm^{-1}, which is in excellent agreement with that deduced by Birge.

† For a more comprehensive discussion the reader should consult the article by K. K. Darrow, "Elementary Notions of Quantum Mechanics," *Rev. Mod. Phys.*, **6**, 23 (1934); also J. C. Slater and N. H. Frank, Introduction to Theoretical Physics, McGraw-Hill Book Company (1933). A very interesting popular discussion of this subject is given by M. Born, The Restless Universe, Chap. 3, Harper and Brothers, New York (1936).

or

$$\frac{p_1}{p_2} = \frac{\sin \theta_2}{\sin \theta_1} = \text{constant.} \tag{8.2}$$

Combining (8.1) and (8.2) it follows that

$$\frac{p_1}{p_2} = \frac{u_2}{u_1}. \tag{8.3}$$

If v_1 and v_2 designate the corpuscular velocity in each medium, it follows from the last equation that

FIG. 8.1. Illustrating Interpretation of Refraction on Basis of Corpuscular Theory.

$$\frac{mv_1}{mv_2} = \frac{u_2}{u_1}. \tag{8.4}$$

That is, the wave (or phase) velocity varies inversely as the particle speed.

Setting $u = \nu\lambda$ and noting, as experiments on interference of light show, that the frequency remains constant in passing from one medium into another, it follows from equation (8.4) that

$$\frac{p_1}{p_2} = \frac{\lambda_2}{\lambda_1}$$

or

$$\underline{\lambda p = \text{constant.}}$$

This, it will be observed, is the relation suggested by de Broglie with the additional postulate that $\lambda p = h$.

The connection between the wave and particle concepts is made even more evident if we compare the Principle of Least Action in dynamics with Fermat's principle in optics. The latter may be stated thus: *The actual path taken by a light ray to pass from any one point, A, to any other given point, B, is that for which the time of transit is a minimum.* That is, if u denote the velocity of the wave motion (phase-velocity),

$$\int_A^B \frac{ds}{u} = \text{minimum.} \tag{8.6}$$

Let us now compare this equation with that which follows from the principle of least action. This principle states that for a system of constant energy E, passing from an initial point A to a final point B, the path followed in accordance with the laws of mechanics will be one for which the integral

$$A = \int_A^B p \cdot ds = \text{minimum,} \tag{8.7a}$$

where p denotes the momentum, and ds is an element of length along the path.

The integral is known as the "Action," and is evidently of the same dimension as h, Planck's constant.   Hence h may be regarded as the *quantum of action.*

Denoting the kinetic energy by T and the potential energy by V,* it follows that for a particle in motion,

$$\tfrac{1}{2}mv^2 = T = E - V$$

and

$$p = mv = \sqrt{2m(E - V)}.$$

Hence equation (8.7a) is also often written in the form

$$A = \int_A^B \sqrt{2m(E - V)}\,ds = \text{minimum.} \tag{8.7b}$$

If a corpuscle in motion behaves under one aspect as a mechanical system, and under the other as a wave motion, its path must be one which satisfied both relations (8.6) and (8.7a).   How can this be interpreted?

According to the theory of relativity, the energy, E, of any particle of mass, m, is given by

$$E = \frac{m_0 c^2}{\sqrt{1 - v^2/c^2}} = m_0 c^2 + \tfrac{1}{2}m_0 v^2 \tag{8.8}$$

to a first approximation, where m_0 is the "rest mass."

The momentum, p, is given, according to the theory of relativity, by the relation

$$p = \frac{m_0 v}{\sqrt{1 - v^2/c^2}} = m_0 v + \tfrac{1}{2}m_0 \frac{v^3}{c^2} + \cdots. \tag{8.9}$$

Hence, according to (8.7a)

$$\int_A^B p \cdot ds = \int_A^B \frac{m_0 c^2}{\sqrt{1 - v^2/c^2}} \cdot \frac{v}{c^2}\,ds = \text{minimum}$$
$$= \int_A^B E \frac{v}{c^2}\,ds = E \int_A^B \frac{v}{c^2}\,ds \tag{8.10}$$
$$= \text{minimum.}$$

Comparing equation (8.10) with (8.6) it follows that

$$u = c^2/v. \tag{8.11}$$

Also, from equations (8.8) and (8.9) it follows that

$$E/p = c^2/v = u, \tag{8.12}$$

* The use here of the symbol V for the potential energy should not be confused with its use to represent the electrical potential in volts.

while

$$dE/dp = v. \tag{8.13}$$

Now to the phase velocity u, associated with the particle speed of magnitude v, we can assign a frequency ν, and wave length λ. To obtain the former, de Broglie postulated the quantum relation

$$\nu = E/h,$$

where E is given by the relativity equation (8.8). In consequence of equation (8.12) it follows that

$$\lambda = u/\nu = E/(p\nu)$$
$$= h/p, \tag{8.14}$$

which is de Broglie's relation.

Furthermore it follows that

$$v = \frac{dE}{dp} = \frac{d(h\nu)}{d(h/\lambda)} = \frac{d\nu}{d\sigma}, \tag{8.15}$$

where $\sigma = 1/\lambda$ = wave number.

This last relation expresses the particle speed in terms of the rate of change with wave number of the frequency of the associated wave motion, and is one which is of considerable importance in the study of wave motion, as shown in the following remarks.

(2) **Group and Phase Velocity**: The equation for the amplitude, y, of an infinite wave train propagated in a single direction (along the positive direction of the x-axis) is given by

$$y = A \cos 2\pi(\nu t - \sigma x), \tag{8.16}$$

where

$$A = \text{maximum amplitude.}$$

Let us consider the result of superposing, on this wave-train, another, of the same amplitude, but slightly different wave number, $\sigma + \Delta\sigma$, and slightly different frequency, $\nu + \Delta\nu$. The amplitude of the resultant wave motion is given by

$$y = A \cos 2\pi(\nu t - \sigma x) + A \cos 2\pi[(\nu + \Delta\nu)t - (\sigma + \Delta\sigma)x],$$
$$= 2A \cos 2\pi(\nu t - \sigma x) \cdot \cos \pi(\Delta\nu \cdot t - \Delta\sigma \cdot x) \tag{8.17}$$

for infinitesimally small values of $\Delta\nu$ and $\Delta\sigma$.

The form of this equation shows that it represents a train of waves whose amplitude varies gradually between the limits zero and $2A$, forming a series of regions of maximum amplitude, separated by regions in which the amplitude decreases to zero. The crest of maximum intensity travels with a velocity v, which is quite different from that of the phase in each wave train. The latter is given by

$$u = \nu/\sigma = \text{phase velocity.} \tag{8.18}$$

From equation (8.17) it follows that y is a maximum for

$$\Delta\nu\cdot t = \Delta\sigma\cdot x.$$

Hence, the velocity, v, of the crest is given by the relation

$$v = \frac{x}{t} = \frac{\Delta\nu}{\Delta\sigma} = \frac{d\nu}{d\sigma} \tag{8.19}$$

in the limit. This defines the *group velocity*, and comparing the last equation with equation (8.15) it is seen that in terms of waves, *the corpuscular speed corresponds to the group velocity*.

That the phase velocity of de Broglie waves exceeds, according to equation (8.11), the velocity of light indicates at once that this velocity has no physical reality—in the sense that it may be measured experimentally. For the velocity at which energy is actually transferred is that given by v, the speed of the crest or "wave packet" formed by superpositions of a large number of monochromatic waves of different frequencies.

Thus we find it possible to reconcile the observations on the corpuscular nature of both photons and electrons with the observations on the wave nature of the same entities on the basis of the relationship between the velocity of a wave packet and the phase velocity of the constituent harmonic waves.

(3) **Principle of Indeterminism**: The association of wave and corpuscular concepts has, however, some very important consequences. In ordinary dynamics a particle of mass m, moving with velocity v, possesses a kinetic energy, $T = \frac{1}{2}mv^2 = E - V$ and momentum $p = mv$. The force acting on the particle is defined by the rate of change of momentum, and a complete solution of the problem is obtained when we are able to derive the position of a particle at any point in space and at any instant of time *from a knowledge of the initial conditions and the forces acting on it*.

On the undulatory point of view, the actual orbit of the particle is replaced by a group of waves ranging in frequency from ν to $\nu + \Delta\nu$, for which the group velocity, v, is the same as that of the corpuscle, while the phase velocity, u, is given by the equation

$$u = \nu\lambda = \frac{h\nu}{p} = \frac{E}{mv} = \frac{E}{\sqrt{2m(E - V)}} \cdot \tag{8.20}$$

Consequently the wave length, $\lambda = h/(mv)$ varies from point to point in space as the field of force varies and the wave is said to be "refracted" in the field of force. Now the energy of the particle must be located in the same region of space as the crest of the group, since, for a monochromatic or plane wave-train extending from $-\infty$ to $+\infty$, it is impossible to locate the energy at any definite point in space between these limits. The exactness with which it is possible to define the position of the particles is therefore limited by the extension in space of the crest of the group of waves. The greater the range of frequencies

which we use in order to form the group, the narrower the extension in space, and therefore the more sharply defined the *position* of the particle.   But this means that in order to define the position accurately we must give up all idea of determining simultaneously, with a similar degree of accuracy, the *velocity*. For the velocity is connected with the wave length by de Broglie's relation, and since we have had to combine a range of frequencies, we can no longer consider that we know the velocity with any degree of exactness.   *The relation is evidently of a reciprocal nature.*   The more sharply we attempt to define the position of the corpuscle at any instant, the greater the range of wave lengths that must be combined to form the group, and consequently the less exactly we can determine the velocity.

We have thus arrived at the conclusion that on the basis of wave concepts it is impossible to determine, simultaneously, the *momentum* and *position* of a corpuscle with the same degree of exactitude, and that there *must exist a definite limitation* upon the accuracy of determination of such pairs of variables.

From this point of view, it follows that when we speak of an energy level in a hydrogen atom and define the corresponding wave-motion by the frequency $\nu = E/h$, we can no longer regard the electron as located at any instant of time at some given point in the orbit.   Since we are dealing with a monochromatic wave, the *electron has no preferred location on the orbit,* and therefore it has the same probability of being found at any instant at any point in the orbit.

This conclusion may be formulated more precisely as the *Principle of Indeterminism*.   This principle, which was first enunciated by W. Heisenberg, constitutes the logical basis for the new method of dealing with problems of atom and electron behavior known as quantum or wave mechanics.

Let us consider two superposed waves of wave lengths λ and $\lambda + \Delta\lambda$ respectively.   The distance between two successive minima (or width of packet), Δx, for the resultant wave, is given by the relation

$$\frac{\lambda}{\Delta x} = \frac{\Delta\lambda}{\lambda}.$$

That is,

$$\Delta x = \lambda^2/\Delta\lambda.$$

In consequence of de Broglie's relation,

$$\Delta p = \Delta(h/\lambda) = h\Delta\lambda/\lambda^2.$$

Hence,

$$\Delta x \Delta p = h. \tag{8.21a}$$

The significance of this result has been stated by J. H. Van Vleck [1] in the following remarks:

" *When dealing with amounts of action comparable with Planck's h, one cannot assign accurate numerical values simultaneously to a coordinate and its corresponding momentum.   Thus, within*

[1] *Chem. Rev.,* **5**, 467 (1928).

the atom, it is meaningless to talk of a simultaneous position and velocity of the electron. It is, of course, possible to attach a meaning to a simultaneous position and velocity of a large body, such as an automobile or even a dust particle, because in such cases we have an enormous number of quanta. Within the atom this is no longer the case. *Experiments may be devised which will determine either x or p accurately, but not both x and p simultaneously.* Instead if Δx be the error in specifying the position x, and Δp that in specifying the momentum p, then the product $\Delta x \Delta p$ of the two errors is always of the order of magnitude of Planck's constant, so that

$$\Delta x \Delta p \sim h.$$

This is the so-called *Heisenberg indeterminism principle*, and, like the second law of thermo-dynamics, is very useful in predicting what experiments are possible, and what are inherently impossible. Thus high precision in position implies low precision in velocity, and vice versa, for the error Δv is of the order $h/m\Delta x$ and therefore increases as we decrease Δx. We may illustrate this in a crude arithmetical way by considering the motion of an electron. If we specify that this electron is exactly at a given position, say the origin, at a given instant $t = 0$, then the error Δx is zero, and consequently the error Δv is infinite; this means that the velocity is inherently undetermined and so can range anywhere from $-\infty$ to $+\infty$; so that at any subsequent instant of time, say one second, there is an overwhelming chance that the electron be an infinite distance away. Suppose, however, that instead of aiming to specify accurately the position of the electron at $t = 0$, we merely say that then it is somewhere between $x = -\frac{1}{2}$ and $x = +\frac{1}{2}$; then $\Delta x = 1$, and Δv is of the order h/m; now $h = 6.55 \times 10^{-27}$, while for an electron $m = 0.9 \times 10^{-27}$ hence the error Δv in velocity is $6.55/0.9$, or about 7 cm./sec. One could then not give accurately a numerical velocity, say 300 cm./sec., but one could say that the velocity lay somewhere between about $296\frac{1}{2}$ and $303\frac{1}{2}$ cm./sec., so that after 1 second the electron would be between about $x = 296$ and $x = 304$. (This is only a very crude calculation; a more accurate study leads to a Gaussian error curve.)

"Another, and better illustration of the Heisenberg indeterminism principle is furnished by an attempt to measure simultaneously both the position and frequency of a packet or wave train of light energy. A prism will record a train of waves as being strictly monochromatic only if the train is infinitely long; the termination of the optical disturbance after a finite time interval will cause an interruption in periodicity and make the light in the prism appear diffuse. If the train contains n waves, it can be shown that the diffuseness in its spectrum will be of the order $1/n$, or in other words the fractional error $\Delta \nu/\nu$ in determining the frequency is comparable with $1/n$. If, following the light quant theory, we assign a packet or "quant" of light a momentum $p = h\nu/c$, then Δp is of the order $h\nu/cn$. On the other hand the length of the wave train is $n\lambda$, where λ is the wave length and consequently the position of the light is indefinite to an extent $\Delta x = n\lambda$. As $\nu = c/\lambda$, the product $\Delta x \Delta p$ of the two errors is of the order of Planck's h.

"Because of the ambiguity resulting from the Heisenberg indeterminism principle, the future of a dynamical system can never be predicted with certainty. Instead only the *probability* that an electron be in a given configuration can be determined, and the future is only statistically determined. This is in sharp contrast to the 'causality principle' of class-ical dynamics, whereby the subsequent history of a dynamical system is determined if we know its initial coördinates and velocities. The uncertainty as to subsequent motion in quantum mechanics is, however, perhaps not due so much to failure of the ordinary cause and effect relation as to the inevitably indeterminate character of the initial conditions, as by the Heisenberg indeterminism principle one cannot give both the initial position and velocity accurately. *Thus quantum mechanics is essentially a means of calculating the probabilities of events.* In a laboratory experiment one performs certain operations and observes certain consequences. The goal of a theory must ever be to explain 'what goes out' in terms of 'what is put in.' At first thought it may appear as if the purely statistical correlation be-tween cause and effect demanded by quantum mechanics is contradictory to the precision with which experiments can be performed. Experiments with large scale quantities, however, involve so many quanta that the Heisenberg indeterminism is obscured, and so there is only

pparently a 'sharp' correlation. On the other hand, our ordinary atomic or molecular experiments are in most cases fundamentally statistical in character, as what is measured is not particular values of the dynamical variables, but rather *average values* of certain functions of these variables, or else *distributions* telling how they are scattered over a wide range of values. Such statistical quantities have a meaning in and can be calculated with quantum mechanics, and so there is no contradiction of Heisenberg's principle."

Amplifying the remarks in the last paragraph let us consider the nature of the information which may be obtained from passing a homogeneous beam of electrons through a slit of width d. The position of any one of the electrons passing through the slit is determined with the accuracy

$$\Delta x = d.$$

But if d is comparable in magnitude with the de Broglie wave length λ, the electrons will be deflected at the edges (diffraction phenomenon). Consequently the emergent beam has a finite angle of divergence θ, which according to the laws of optics, is determined by the relation

$$\sin \theta = \frac{\lambda}{d} = \frac{\lambda}{\Delta x}$$

and the uncertainty in momentum of the electrons in a direction parallel to the length Δx after passing the slit is given by

$$\Delta p = \frac{h}{\lambda} \sin \theta = \frac{h}{\lambda} \cdot \frac{\lambda}{\Delta x}.$$

That is,

$$\Delta p \Delta x = h.$$

As another illustration let us consider the following experiment for determining the instantaneous position of an electron in motion. In order to see the electron it must be illuminated, and from the theory of optical instruments it is known that for an ideal lens the uncertainty Δx in the determination of x (see Fig. 8.2) is

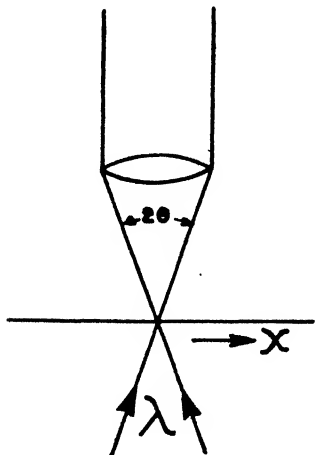$$\Delta x = \frac{\lambda}{\sin \theta},$$

FIG. 8.2.   Illustrating the Principle of Indeterminism

where λ is the wave length of light used and 2θ is the aperture of the lens. In order to minimize the value of Δx, λ should be chosen as small as possible, and θ as large as possible. Theoretically, gamma rays could be used. To make an observation, at least one photon must be scattered by the electron and pass through the lens to the detector. But, in consequence of the Compton effect, the electron receives a recoil, and the ex-

act amount of this recoil cannot be determined since the lens receives in the same focus all the rays originating in the angle 2θ. Hence the uncertainty in the magnitude of the momentum of the electron in the x-direction is given by

$$\Delta p \geqslant \frac{h}{\lambda} \sin \theta.$$

The inequality sign indicates that the magnitude of the uncertainty will never be less than $h \sin \theta/\lambda$, but may be greater, owing to physical imperfections in the experimental arrangement. Consequently,

$$\Delta x \Delta p \geqslant h. \tag{8.21b}$$

To decrease the magnitude of Δp, we might use radiation of very long wave length (e.g., infra-red). In fact, we might measure the velocity (and hence p) by means of the Doppler effect; but obviously this would increase the value of Δx, and the result regarding the value of $\Delta p \Delta x$ would never be less than that given by equation (8.21).

A similar relation is valid for the simultaneous determination of energy and time in the form

$$\Delta E \Delta t \geqslant h. \tag{8.22}$$

Thus, given an absolutely monochromatic wave (for which therefore $\Delta E = 0$), then, as pointed out in the quotation from Van Vleck, the wave-train must be infinitely long, and therefore the uncertainty in t is infinitely great. The representation of a particle, moving with momentum mv, by a wave-packet, necessarily leads to an indetermination in the position of the particle if mv is known very accurately. "For the use of wave-groups," as Bohr has stated,[*] "is necessarily accompanied by a lack of sharpness in the definition of period and wave-length, and hence also in the definition of the corresponding energy (E) and momentum (p) as given by the relation

$$E/\nu = p\lambda = h.$$

"Rigorously speaking, a limited wave-field can be obtained only by a superposition of a manifold of elementary waves corresponding to all values of ν. But the order of magnitude of the mean difference between these values for two elementary waves in the group is given in the most favorable case by the condition

$$\Delta t \Delta \nu = \Delta x \Delta \sigma = 1."$$

From this, equation (8.22) follows directly.

From this point of view the model of the hydrogen atom introduced by Bohr cannot be regarded as anything more than a very crude approximation. According to this theory, which is discussed in the following section, the hydrogen

---

[*] N. Bohr, *Nature*, **121**, 850 (1928).

atom is represented as constituted of an electron revolving in a periodic orbit (circular or elliptical) about the proton under the interaction of a coulomb force of attraction, and a centripetal force. The dimensions of the orbit and frequency of revolution are calculated by application of Newtonian mechanics as modified by certain quantum conditions postulated to yield the observed spectral lines.

But is it possible to observe the orbit of an electron in a hydrogen atom? The answer must be in the negative, because, as pointed out in the previous paragraphs, *whatever experiment we devise to make such an observation will "spoil" the system.* As Bohr has remarked in the address mentioned above:

"Our usual description of physical phenomena is based entirely on the idea that the phenomena concerned may be observed, without disturbing them appreciably. . . . Now the quantum postulate implies that any observation of atomic phenomena will involve an interaction with the agency of observation not to be neglected. . . . Just as the relativity theory has taught us that the convenience of distinguishing sharply between space and time rests solely on the smallness of the velocities ordinarily met with compared to the velocity of light, we learn from the quantum theory that the appropriateness of our usual causal space-time description depends entirely upon the small value of the quantum of action as compared to the actions involved in ordinary sense perceptions."

As a consequence the new atom-mechanics enables us, as stated in the quotation from Van Vleck, to calculate only probability distribution functions, for both the position and velocity of any corpuscle. Instead of calculating the orbit of an electron in an atomic system we deduce by the mathematical technique of the new theory a function which expresses the probability of occurrence of the electron per unit volume at any given point in the space located about the nucleus. Similarly it is possible to calculate a probability distribution function for the momentum of the electron.

This lack of precision in determination of definite "orbits" is of course a consequence of the fact that the Action ($\int pds$ taken over the complete orbit) is of the order of magnitude of h. As however, this integral increases to values which are very large compared to Planck's constant, the spread of the probability distribution functions becomes narrower until when we come to deal with macroscopic systems, these distribution functions assume the definite values which are deduced by the methods of ordinary dynamics. That is, *for large-scale phenomena, quantum mechanics leads to the same conclusions as classical mechanics*, because the degree of inexactness deduced by the former becomes inappreciable in comparison with the experimental limitations.

(4) **The Schroedinger Equation:** In this section we shall describe briefly the method devised by E. Schroedinger for calculating the probability distribution functions, which, as stated already, replace in the new theory the more concrete models of electronic orbits postulated in the Bohr theory.

As stated previously a typical equation for a harmonic wave has the form

$$y = A \cos 2\pi(\nu t - \sigma x) \qquad (8.16)$$

which represents the *amplitude*, y, as a function of x and t. This evidently

corresponds to a wave propagated in the positive direction of the x-coordinate, since an increase in x is equivalent to an increase in t. By changing the origin to a distance $x = \frac{1}{4}\lambda$, this equation becomes

$$y = A \sin 2\pi(\nu t - \sigma x).$$

The equations

$$y = A \sin 2\pi(\nu t + \sigma x)$$

and

$$y = A \cos 2\pi(\nu t + \sigma x).$$

correspond to waves propagated in the negative direction of x, that is, from right to left.

By differentiating any one of these four equations twice with respect to t alone, and also twice with respect to x alone, we obtain the partial differential equations for wave motion:

$$\frac{\partial^2 y}{\partial x^2} = -4\pi^2\nu^2 y \tag{8.22}$$

and

$$\frac{\partial^2 y}{\partial t^2} = -4\pi^2\sigma^2 y. \tag{8.23}$$

Hence

$$\frac{\partial^2 y}{\partial x^2} = \frac{\sigma^2}{\nu^2}\frac{\partial^2 y}{\partial t^2} = \frac{1}{u^2}\frac{\partial y^2}{\partial t^2}, \tag{8.24}$$

where

$$u = \nu/\sigma = \nu\lambda.$$

This last equation represents the vibration of a stretched string and is usually derived directly by considering the forces acting on an element of length of the string.*

The general solution of equation (8.24) has the form

$$y = f(x)g(t), \tag{8.25}$$

where $f(x)$ is a function of x alone, and $g(t)$ of t alone, and the two functions satisfy the respective *ordinary* differential equations

$$\frac{d^2 f(x)}{dx^2} + s^2 f(x) = 0 \tag{8.26}$$

and

$$\frac{d^2 g(t)}{dt^2} + s^2 u^2 g(t) = 0 \tag{8.27}$$

in which s^2 is an arbitrary constant (the square being used to indicate that it is always positive).

These equations are evidently analogous to equations (8.22) and (8.23) respectively. While a solution of each of these equations can be written in

---

* This derivation is given in books on acoustics. See also S. Dushman, Elements of Quantum Mechanics, p. 31, John Wiley and Sons, New York (1938). (Ref. S. D.) The mathematical discussion given in the following section is taken from pp. 34–41.

the form of a combination of sine and cosine functions, it is much more convenient to use the relations between these and the exponential functions,

$$e^{isx} + e^{-isx} = 2 \cos sx, \tag{8.28}$$

$$e^{isx} - e^{-isx} = 2 i \sin sx, \tag{8.29}$$

where

$$i = \sqrt{-1}.$$

In terms of these exponentials the solutions of equations (8.26) and (8.27) are as follows:

$$f(x) = A e^{isx} + B e^{-isx}, \tag{8.30}$$

$$g(t) = C e^{isut} + D e^{-isut}, \tag{8.31}$$

where A, B, C and D are four arbitrary constants, the values of which are determined in any particular case by the "initial" and "boundary" conditions.

Since the application of these solutions to the case of a stretched string fastened at both ends illustrates certain fundamental properties of the Schroedinger equation we shall consider this case at further length.

For $x = 0$ and $x = L$ (where L = length of string), $f(x) = 0$. (These are known as the "boundary" conditions.) Hence it follows from equation (8.30) that

$$A = -B.$$

Also

$$\begin{aligned} f(x) = 0 &= A(e^{isL} - e^{-isL}) \\ &= 2Ai \sin sL. \end{aligned}$$

Hence $\sin sL = 0$, which indicates that

$$sL = n\pi; \qquad s = n\pi/L, \tag{8.32}$$

where $n = 1, 2, 3$, etc.

Thus, the particular solution of equation (8.30) is

$$f(x) = 2Ai \sin (n\pi x/L).$$

Since $f(x)$ must be real in the case of a vibrating string, A must be a pure imaginary, and therefore $Ai = A_0$, a real quantity. Hence, the last equation should be written

$$f(x) = 2A_0 \sin (n\pi x/L). \tag{8.33}$$

More generally, if A is a complex quantity, that is, of the form $ai + b$, then $f(x)$ will designate a complex quantity of which the complex conjugate is denoted by $\bar{f}(x)$. In this case $f(x)\bar{f}(x)$ is a real quantity, the value of which is given by the relation

$$f(x)\bar{f}(x) = 4|A|^2 \sin^2 (n\pi x/L),$$

where the vertical lines indicate a product of the form

$$(a + bi)(a - bi) = a^2 + b^2,$$

that is, a real quantity.

Since $f(x)$ denotes the amplitude of the wave at any instant as a function of x, $f(x)\bar{f}(x) = |f(x)|^2$ corresponds to the *intensity*. Thus, whether $f(x)$ is complex or real, the *intensity is always a real magnitude*.

In the case of equation (8.31), we assume $g(t) = 0$ for $t = 0$. Consequently $C = -D$, and the solution assumes the form

$$g(t) = 2Ci \sin sut$$
$$= 2C_0 \sin (n\pi ut/L). \qquad (8.34)$$

Since the string is fastened at both ends, these two points ($x = 0$, and $x = L$) must constitute nodes. Hence $L = \dfrac{n\lambda_n}{2}$ where λ_n is the wave length associated with any given value of n. For $n = 1$, $\lambda = 2L$ and this corresponds to the *fundamental* frequency, $\nu = u/\lambda = u/(2L)$. The frequency $\nu_n = u/\lambda_n = nu/(2L) = n\nu$ corresponds to the nth normal mode of vibration of the string. In terms of frequency and wave length, equations (8.33) and (8.34) assume the forms:

$$f_n(x) = 2A_0 \sin 2\pi x\sigma_n, \qquad (8.35)$$

$$g_n(t) = 2C_0 \sin 2\pi \nu_n t, \qquad (8.36)$$

where $\sigma_n = 1/\lambda_n$, and the subscript n designates the corresponding harmonic.

Since the sum of any finite number of particular solutions of a differential equation is also a solution, we can obtain a more general solution in the form

$$f(x) = f_1(x) + f_2(x) + \cdots + f_n(x)$$
$$= 2 \sum_{n=1} A_n \sin 2\pi n\sigma x$$

and similarly for $g(t)$.

It will be observed that the differential equations (8.26) and (8.27) have *physically significant solutions only for those discrete values of s which are defined by equation* (8.32). These are known as *characteristic values* or *eigenvalues*, and the corresponding values of the functions $f_n(x)$ and $g_n(t)$, as defined in equations (8.35) and (8.36) are known as *characteristic functions* or *eigenfunctions*.

Equation (8.24) represents the partial differential equation for a wave motion in one dimension. In the case of a stretched membrane in vibration it can be shown that the partial differential equation for the vibrations is given by

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} - \frac{1}{u^2} \cdot \frac{\partial^2 \psi}{\partial t^2} = 0.$$

For sound waves in three dimensions, the fluctuation in pressure at any point is given by the equation,

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} - \frac{1}{u^2} \cdot \frac{\partial^2 \psi}{\partial t^2} = 0,$$

which is usually written in the form

$$\nabla^2\psi - \frac{1}{u^2} \cdot \frac{\partial^2\psi}{\partial t^2} = 0,$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{8.37}$$

is known as the *Laplacian operator*.

So far we have dealt with the partial differential equation for a wave motion in which u, the phase velocity, is *constant*. However, as deduced above, the phase velocity for de Broglie waves is given by the relation*

$$u = \frac{E}{\sqrt{2m(E - V)}} \tag{8.20}$$

and the wave length, by

$$\lambda = \frac{h}{mu} = \frac{h}{\sqrt{2m(E - V)}} \cdot \tag{8.38}$$

In these equations, E, the total energy, is a constant, while V, the potential energy, is a function of the coordinates. Consequently both the phase velocity and wave length of the de Broglie waves will vary from point to point in the field of force in which the particle is moving.

Now let us consider first, equation (8.24). As mentioned above, a solution of this is obtained by taking the product of a function of x alone, which we shall designate by $\phi(x)$, and of another which involves only t. The latter is represented in quantum mechanics (for certain valid reasons) by $e^{-2\pi i\nu t}$. Consequently the *partial* differential equation reduces to the *ordinary* differential equation

$$\frac{d^2\phi}{dx^2} + \frac{4\pi^2\nu^2}{u^2}\,\phi = 0,$$

that is,

$$\frac{d^2\phi}{dx^2} + \frac{4\pi^2}{\lambda^2}\,\phi = 0. \tag{8.39}$$

Substituting for λ from equation (8.38), we obtain the relation

$$\frac{d^2\phi}{dx^2} + \frac{8\pi^2 m}{h^2}\,(E - V)\phi = 0. \tag{8.40}$$

This is the famous *Schroedinger differential equation* for the one-dimensional case. In the case of three dimensions, the expression for the Schroedinger equation is of the form

$$\nabla^2\phi + \frac{8\pi^2 m}{h^2}\,(E - V)\phi = 0, \tag{8.41}$$

---

* See footnote, p. 215.

where the Laplacian operator is expressed in terms of rectangular coordinates by equation (8.37). If, however, spherical coordinates are used, or some other type of coordinate system, the expression for the operator becomes much more complicated.

Since, in general, V is a function of the coordinates, equation (8.40) or (8.41) has a solution of the form $\phi(x, y, z)$. What is of interest is the significance of this function in relation to problems of atomic structure or electronic behavior. In the case of a vibrating string fastened at both ends, the solution is of the form

$$y = A(e^{isx} \pm e^{-isx}),$$

where $s = n\pi/L$, y represents the amplitude of vibration, and y^2, the *intensity*. How may we apply this interpretation to the case of the solution, ϕ, of the Schroedinger equation?

To answer this question let us consider the relatively simple problem of an electron confined to *move* between two potential barriers, which is illustrated in Fig. 8.3. The potential energy has the value $V = 0$ for the region extending from $x = -a$ to $x = +a$, and has the value V_0, outside this region.

Hence, the Schroedinger equation has the form

$$\frac{d^2\phi_1}{dx^2} + \frac{8\pi^2 m}{h^2} E\phi_1 = 0 \tag{8.42}$$

for the region $x = -a$ to $x = +a$, and the form

$$\frac{d^2\phi_2}{dx^2} + \frac{8\pi^2 m}{h^2}(E - V_0)\phi_2 = 0 \tag{8.43}$$

for the regions designated II and III in the diagram. The subscripts for ϕ are used to indicate that the solution of the Schroedinger equation will not necessarily be of the same form in the two cases.

Let us furthermore consider the solutions for which $V_0 > E$. Since E is positive (the electron has this kinetic energy in region I), $E - V_0$ is *negative*.

Let

$$\alpha^2 = 8\pi^2 mE/h^2 \tag{8.44}$$

and

$$\beta^2 = 8\pi^2 m(V_0 - E)/h^2. \tag{8.45}$$

Then equations (8.42) and (8.43) take the forms

$$\frac{d^2\phi_1}{dx^2} + \alpha^2\phi_1 = 0, \tag{8.46}$$

and

$$\frac{d^2\phi_2}{dx^2} - \beta^2\phi_1 = 0. \tag{8.47}$$

We now introduce the boundary conditions which have to be satisfied by ϕ_1 and ϕ_2 in order that the solutions shall be *physically significant*.

The first condition is that at $x = \pm a$, $\phi_1 = \phi_2$. This is known as the *continuity relation.* The value of ϕ must not exhibit any abrupt discontinuity at any point in the region under consideration.

The second condition is that there shall be no discontinuity in the *slope.* That is, at $x = \pm a$,

$$\frac{d\phi_1}{dx} = \frac{d\phi_2}{dx} .$$

The general solution of equation (8.46) is

$$\phi_1 = Ae^{i\alpha x} + Be^{-i\alpha x},$$

and from symmetry conditions it follows that $A = \pm B$.

Hence

$$\phi_1 = 2A \cos \alpha x \tag{8.48}$$

or

$$= 2Ai \sin \alpha x. \tag{8.49}$$

The general solution of equation (8.47) is

$$\phi_2 = Ce^{\beta x} + De^{-\beta x},$$

which represents a combination of two *exponential* functions.
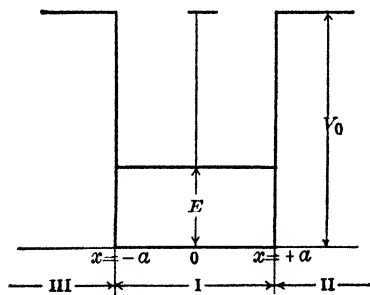
Fɪɢ. 8.3.   Illustrating Behavior of Electron in Potential "Box"

For positive values of x, the first one of these increases rapidly, while the other one decreases rapidly with increase in value of x. From the point of view of physical interpretation, as will be evident from the subsequent remarks, only the second function ($De^{-\beta x}$) can be used, and similar considerations indicate that for negative values of x, only the first function has any sense. Furthermore it follows again from symmetry considerations that $C = \pm D$.

If now we introduce the conditions for continuity in both the values of ϕ and of $d\phi/dx$, it may be shown that equations (8.46) and (8.47) are satisfied by the following sets of eigenfunctions, where the subscripts refer to the three different regions shown in Fig. 8.3.

Group I:

$$\left.\begin{array}{ll} \phi_I = 2A \cos \alpha x & (- a \leqslant x \leqslant a) \\ \phi_{II} = 2A \cos \alpha a \cdot e^{-\beta(x-a)} & (x > a) \\ \phi_{III} = 2A \cos \alpha a \cdot e^{\beta(x+a)} & (x < - a) \end{array}\right\} . \tag{8.50}$$

Group II:

$$\left.\begin{array}{ll} \phi_I = 2iA \sin \alpha x & (- a \leqslant x \leqslant a) \\ \phi_{II} = 2iA \sin \alpha a \cdot e^{-\beta(x-a)} & (x > a) \\ \phi_{III} = 2iA \sin \alpha a \cdot e^{\beta(x+a)} & (x < - a) \end{array}\right\} . \tag{8.51}$$

Group I represents functions characterized by the property that ϕ remains unaltered in sign with change in sign of x. These are therefore designated *symmetrical functions* (see Fig. 8.4), while those in Group II, which change sign with x, are known as *antisymmetrical functions*. (See Fig. 8.5.)

That is, we shall have set up in the "box" two sets of *stationary wave patterns*, just as in the case of a vibrating string.

Now in quantum mechanics the amplitude function, ϕ, has no physical significance, since we are not dealing with a wave motion transmitted through a medium. All that the electron diffraction measurements indicate is that it is possible to assign to the electrons a wave length. However, since $\phi\bar{\phi}$ is always real, we *interpret this product as a measure of the probability of occurrence of the electron per unit length along the axis of x.*

Fig. 8.4. Symmetrical Eigenfunctions for Electron in "Box"

From this point of view it is seen from equations (8.50) and (8.51) that $\phi\bar{\phi}$ has a finite value even in the regions outside the barriers. In other words, there exists a *definite probability of penetration of electrons into regions for which V is greater than E.* This is a deduction which is quite at variance with classical mechanics, since in the latter, V can never exceed E. The conclusion is, however, in accord with the Principle of Indeterminism, which denies the possibility of associating definite position with precise knowledge of momentum.

This penetration is indicated by the "tails" on the trigonometric functions plotted in Fig. 8.4 and Fig. 8.5. As V increases and tends to approach infinitely high values, β increases and hence, for any given value of $x(x > a$ or $< -a)$, the magnitude of the exponential factor, in the expression for ϕ_{II} or ϕ_{III}, decreases and ultimately becomes equal to zero.

Fig. 8.5. Antisymmetrical Eigenfunctions for Electron in "Box"

Hence, we have the result,

$$\cos \alpha a = 0 = \sin \alpha a. \tag{8.52}$$

From the relation $\cos \alpha a = 0$, which applies to the symmetrical functions, it follows that

$$\alpha a = \frac{\pi}{2}(2n + 1),$$

where $n = 0, 1, 2 \cdots$.

From the relation $\sin \alpha a = 0$, which applies to the antisymmetrical functions, we deduce the relation
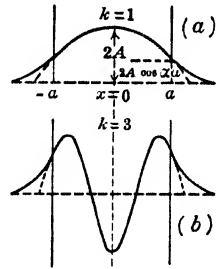
$$\alpha a = \frac{\pi}{2}2n.$$
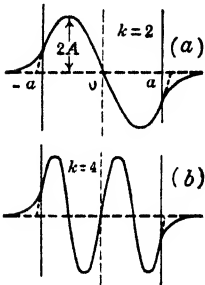
Thus, for both cases,

$$\alpha a = k\pi/2, \tag{8.53}$$

where $k = 0, 1, 2 \cdots$.

Substituting for α from equation (8.44), it follows that:

$$E_k = \left(\frac{k}{2a}\right)^2 \frac{h^2}{8m} . \tag{8.54}$$

That is, for an electron in a potential box the total energy cannot vary continuously from $E = 0$. Rather, *the electron possesses a series of discrete energy states, each of them being associated with a quantum number k* in accordance with equation (8.54). These constitute the eigenvalues of the system, and the corresponding eigenfunctions, ϕ_k, will each be represented by a simple harmonic stationary wave pattern such that the number of nodes (excluding those at the walls) is equal to $k - 1$, as shown in Figs. 8.4 and 8.5. These eigenfunctions may be expressed in the form

$$\phi_S = 2A \cos \frac{2\pi x}{\lambda}$$

or

$$\phi_A = 2Ai \sin \frac{2\pi x}{\lambda},$$

where $\lambda = h/\sqrt{2mE_k} = 4a/k$, and ϕ_S and ϕ_A designate symmetrical and anti-symmetrical functions respectively.

The analogy between these results and those deduced for a vibrating string is self-evident.

For the more general case in which V_0 is not infinitely great, the solutions are of the same nature. Only in this case the eigenvalues will correspond to values of the de Broglie wave length which are given by $4a'/k$ where, as is evident from Figs. 8.4 and 8.5, a' is greater than a, the difference increasing with decrease in the value of V_0. This follows from the fact that the intercepts, $\cos \alpha a$ or $\sin \alpha a$, increase as V_0 decreases.

Let us now consider further the physical interpretation of $\phi\bar{\phi}$. According to the quantum mechanics point of view $\bar{\phi}\phi dx$ is interpreted as a measure of the probability of occurrence of the electron in an element dx at the point x. In the present case ($V_0 \rightarrow \infty$),

$$\phi_S\bar{\phi}_S = 4A^2 \cos^2 \alpha x,$$

$$\phi_A\bar{\phi}_A = 4A^2 \sin^2 \alpha x.$$

If we start with the fact that there is an electron in the box, it is possible to determine the value of A which will lead to the value unity for the total prob-

ability of finding the electron in the box. Consequently

$$1 = \int \phi_S \bar{\phi}_S dx = \int_{-a}^{a} 4A^2 \cos^2 \alpha x \, dx$$

$$= 4A^2 \int_{-a}^{a} \cos^2 \frac{2\pi x}{\lambda} \, dx = 4A^2 \frac{\lambda}{2\pi} \int_{0}^{k\pi} \cos^2 \theta \, d\theta,$$

where $\theta = 2\pi x/\lambda$, and the limits $x = -a$ to $x = +a$, correspond to a change in θ from $\theta = 0$ to $\theta = 4\pi a/\lambda = k\pi$.

Since

$$\int_{0}^{k\pi} \cos^2 \theta \, d\theta = k \int_{0}^{\pi} \cos^2 \theta \, d\theta = k\pi/2,$$

$$1 = 4A^2 \frac{\lambda}{2\pi} \cdot \frac{k\pi}{2} = 4A^2 \frac{k\lambda}{4}$$

and hence

$$2A = \frac{2}{\sqrt{k\lambda}} = \frac{1}{\sqrt{a}} .$$

The same result is, of course, deduced from a consideration of $\phi_A \bar{\phi}_A dx$. Hence, the so-called *normalized forms of the eigenfunctions* are given by the relations,

$$(\phi_S)_k = \frac{1}{\sqrt{a}} \cos (2\pi x/\lambda_k), \tag{8.55}$$

$$(\phi_A)_k = \frac{i}{\sqrt{a}} \sin (2\pi x/\lambda_k), \tag{8.56}$$

which may obviously be expressed in terms of E_k instead of λ_k.

From equation (8.54) it follows that a plot of E_k versus k will be represented by a series of discrete points on a parabola, and that the distance between any two adjacent energy levels, as well as the total spread of the levels will increase with decrease in the value of $L = 2a$, the width of the box.

Substituting the values adopted for h and m, in equation (8.54) this takes the form

$$\left. \begin{aligned} E_k &= (k/L)^2 \times 6.022 \times 10^{-27} \text{ erg} \\ &= (k/L)^2 \times 3.759 \times 10^{-15} \text{ abs. volt.} \end{aligned} \right\} \tag{8.57}$$

For $L = 2$ cm.:

$$E_k = k^2 \times 9.40 \times 10^{-16} \text{ electron volt,}$$

while, for $L = 2 \times 10^{-8}$ cm.,

$$E_k = k^2 \times 9.40 \text{ electron volts.}$$

That is, in the lowest energy state for an electron in a potential "box" of atomic width, the kinetic energy has a value of 9.40 electron volts, and the as-

sociated de Broglie wave length for an infinitely high potential barrier is 4×10^{-8} cm.

Now in the case of an electron held in an atomic system by the attractive force due to the nucleus, or positively charged kernel, we may in a sense regard the electron as confined in a potential box of the order of 2×10^{-8} cm. in width. Therefore we can expect to observe energy levels of which the lowest is of the order of several electron volts, and the fact that the observed ionization energies range for the different elements from 3.9 e.v. (for cesium) to 24.5 e.v. (for helium) is thus in agreement with this conclusion.

In a solid there actually exist three sets of potential barriers, one for each direction of coordinates. The determination of the discrete energy levels for this case is of special interest in the theory of the solid state. In order to simplify the problem let us assume that the atoms are all alike and arranged at the corners of a simple cubic lattice. Let $2L$ denote the side of the cube, and again let us assume $V = 0$ in the region $x = y = z = \pm L$, and that V is infinitely great midway between any pair of adjacent atoms. (Therefore there can be no penetration of electrons from one atom to another, and the substance would constitute an ideal insulator.)

The Schroedinger equation, in terms of rectangular coordinates, is

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} + \frac{\partial^2 \phi}{\partial z^2} + (E - V)\phi = 0.$$

The resulting form for ϕ is that of a product of the separate solutions for each direction of coordinates, that is,

$$\phi = \sin \frac{\pi l_1 x}{L} \sin \frac{\pi l_2 y}{L} \sin \frac{\pi l_3 t}{L} , \qquad (8.58)$$

where l_1, l_2 and l_3 are integers and the origin of coordinates is taken at a point which is in the center of the cube of side equal to $2L$.

The corresponding discrete energy values are given by the relation

$$E_{l_1 l_2 l_3} = \frac{h^2}{8m} \left(\frac{l_1{}^2 + l_2{}^2 + l_3{}^2}{L^2} \right) . \qquad (8.59)$$

In this case, it will be observed that it is possible to have more than one energy state for the same value of $E = E_0$. Technically the state is said to be of the *degenerate* type. (This will be discussed more fully in a subsequent section.) Thus we can have the three states E_{211}, E_{121} and E_{112} for which E has the same value, but the eigenfunctions are different.

For any given value of $E = E_0$ all the energy states will be represented by points on a sphere of radius

$$r = \sqrt{8mL^2 E_0/h},$$

and it follows that the *total number* of states, N, for which the energy is equal

to or less than E_0 will be given by the volume of an octant of the sphere, since each set of positive integers corresponds to a certain state. Hence

$$N = \frac{\pi r^3}{6} = \frac{8\pi}{6}\left(\frac{2mL^2E_0}{h^2}\right)^{3/2}. \tag{8.60}$$

This result is important in connection with the electron theory of the solid state, and the most recent views on the nature of the differences between conductors and non-conductors.

We can now consider the more general case in which V and consequently the de Broglie wave length are functions of the n coordinates q_1, q_2, $\cdots$, q_n. The solution, ϕ, has the mathematical significance of the amplitude of a wave motion in the n-dimensional space, and therefore has no physical interpretation. But such an interpretation is obtained if we regard $\bar\phi\phi dq_1 dq_2 \cdots dq_n$, as a measure of the probability that the system will occur in the element of "volume," $dv = dq_1 dq_2 \cdots dq_n$.

Now if we furthermore place the commonsense restrictions (equivalent to boundary conditions) on $\bar\phi\phi$, that it must be a finite, single-valued, and continuous function of the coordinates, then we find that "sensible" solutions are obtained only for a certain series of discrete values of E. These are the values of the energy states postulated by the Bohr theory, and the validity of the results obtained by solving the Schroedinger equation can thus be tested by comparison with the results of observations.

9. The Bohr-Sommerfeld Theory of Electronic Orbits

(1) **Bohr's Derivation of the Rydberg Constant:** As mentioned in a previous section, Bohr suggested, in 1913, the view that spectral lines arise from transitions between energy levels in accordance with the frequency relation

$$\nu_{ij} = \frac{E_i - E_j}{h},$$

where ν_{ij} is the frequency of (monochromatic) radiation emitted as a result of a transition from the upper state defined by energy E_i to the lower one defined by energy E_j. This suggestion proved to be one of the most fruitful concepts in the history of physics. It opened up the whole field of spectroscopic observations to satisfactory interpretation and as a result it has been found possible not only to formulate definite models of the electron configurations of the different atomic species, but also to interpret on this basis the occurrence of periodic properties of elements.

It was but natural that Bohr should attempt to develop a more definite "picture" of atomic structure by means of which the actual energy values of the different stationary states (corresponding to spectroscopic terms) might be calculated. The model which he postulated involved the application of two separate assumptions. Firstly, in view of the existence of a Coulomb force of

attraction between any one electron in an atomic system and the nucleus, the analogy with cosmic systems leads to the conclusion that the electrons must describe periodic orbits about the nucleus, the constants of which may be calculated by the methods of classical dynamics. Secondly, the observations on the existence of discrete energy states, corresponding to certain permitted orbits, necessitate the introduction of *quantizing conditions.*

Let us consider the case of the simplest atom, that of hydrogen, and in order to generalize the problem slightly we shall assume an electron of charge e revolving in a *circular* orbit about a nucleus of charge Ze, where Z represents the number of units of positive charge on the nucleus.*

Let v = velocity of electron in orbit, $2a$ = diameter of orbit, ω = frequency of revolution. Then

$$v = 2\pi a \omega.$$

$$\text{Force of attraction} = \frac{Ze^2}{a^2}. \tag{9.1}$$

$$\text{Centrifugal force} = \frac{mv^2}{a} = ma(2\pi\omega)^2, \tag{9.2}$$

where m = the mass of the electron.

Since the force of attraction must be equal to the centrifugal force, it follows from (9.1) and (9.2) that

$$\omega^2 = \frac{Ze^2}{4\pi^2 ma^3}. \tag{9.3}$$

Now the total energy, E, of the system is made up of the kinetic energy (T) and potential energy (V) of the electron in the orbit.

But

$$T = \tfrac{1}{2}mv^2 = \tfrac{1}{2}m(2\pi\omega a)^2 = \frac{Ze^2}{2a}. \tag{9.4}$$

Also

$$V = \int_{\infty}^{a} \frac{Ze^2}{r^2}\, dr = -\frac{Ze^2}{a}, \tag{9.5}$$

where r is the distance between nucleus and electron.

Hence

$$E = T + V = -\frac{Ze^2}{2a}. \tag{9.6}$$

It will be observed that the potential energy is negative and equal to twice the total energy. That is

$$T = -\tfrac{1}{2}V = -E = W,$$

* If additional electrons, other than the one under consideration, surround the nucleus; then Z is the "effective nuclear charge" (cf. p. 249).

where *W is the total amount of energy required to remove the electron to infinite distance.* These conclusions may be shown to be true for any Coulomb field of force, and therefore for the case of elliptic as well as circular orbits. In the former case, $2a$ denotes the major axis of the ellipse.

The reason for the negative value of E_p is evident when it is considered that the force acting on the electron at infinite distance is zero and *increases* as r, the distance between electron and nucleus, is *decreased.* Hence, if the potential energy is put equal to zero at $r = \infty$, it must be made more and more negative as r is decreased.

Now let us write

$$W = -E = \frac{Ze^2}{2a},$$

that is,

$$2a = \frac{Ze^2}{W}. \tag{9.7}$$

Then it follows from equations (9.3) and (9.7) that

$$\omega = \sqrt{\frac{2W^3}{\pi^2 e^4 m Z^2}}. \tag{9.8}$$

These relations give the diameter of the orbit and frequency of revolution of the electron in its orbit in terms of the total energy $W = -E$.

So far no assumptions have been made regarding the manner in which the discrete stationary states are determined. According to classical electrodynamics, the electron revolving in an orbit with frequency ω would emit radiation of the same frequency, which in turn would cause the orbital diameter to decrease and the value of ω to increase continuously until finally the electron would fall into the nucleus. But the atom is a stable system, and according to Bohr's postulate, emission of radiation occurs only as the atomic system passes from one particular state of energy, E_n, to another of energy, E_m, and then the radiation emitted is monochromatic and of frequency

$$\nu = \frac{E_n - E_m}{h}.$$

It is therefore necessary to introduce some quantum condition by which the different possible values of E shall be determined for the different states. Accordingly Bohr postulated in his very first paper that the various orbits are defined by the condition that for any one of them the *angular momentum of the electron in its orbit must be an integral value of $h/2\pi$*, that is

$$p_n = mv_n a_n = \frac{nh}{2\pi}, \tag{9.9}$$

where p_n = angular momentum of electron in nth orbit, a_n = radius of nth orbit, and n is known as the *quantum number*.

The deeper significance of this assumption will be discussed below. For the present let us consider the consequences of introducing the quantizing condition defined by equation (9.9)

From equations (9.4) and (9.9) it follows that

$$mva_n = \tfrac{1}{2}mv^2 \cdot \frac{2a_n}{v} = \frac{T}{\pi\omega} = \frac{W_n}{\pi\omega} = \frac{nh}{2\pi} \cdot$$

Hence

$$\omega = \frac{2W_n}{nh} \cdot \tag{9.10}$$

Eliminating ω between equations (9.8) and (9.10) it follows that

$$W_n = \frac{2\pi^2 e^4 m Z^2}{n^2 h^2} \cdot \tag{9.11}$$

From this it follows that in the transition from a state of higher energy level $W_n = -E_n$ to that of lower energy level, $W_k = -E_k$, the frequency of radiation *emitted* is given by

$$\nu = \frac{E_n - E_k}{h} = \frac{W_k - W_n}{h}$$
$$= \frac{2\pi^2 e^4 m Z^2}{h^3} \left\{ \frac{1}{k^2} - \frac{1}{n^2} \right\} \cdot \tag{9.12}$$

Also, in the transition of the system in the reverse direction the frequency of radiation *absorbed* is given by the same relation.

It is evident that equation (9.12) may be written in the form

$$\nu = Z^2 Rc \left\{ \frac{1}{k^2} - \frac{1}{n^2} \right\}, \tag{9.13}$$

where

$$R = \frac{2\pi^2 e^4 m}{ch^3} \cdot \tag{9.14a}$$

Substituting for e, m, h and c the best values available at that time, Bohr deduced a value of R which agreed remarkably well with the value of the Rydberg constant obtained from spectroscopic observations.

Actually the relatively small differences between the value of R deduced by means of equation (9.14a) and those observed spectroscopically for hydrogen and helium may be accounted for very simply. In deriving the above equations the assumption was made that the electron revolves about a stationary nucleus. This would, however, be valid only if the latter had infinite mass. According

to ordinary dynamics the electron of mass, m, and the nucleus of finite mass, M, rotate about their center of mass, with the result that in equation (9.14a) m should be replaced by the *reduced mass*

$$\mu = \frac{mM}{m + M}.$$

Introducing this correction the result obtained is

$$R = R_\infty/(1 + m/M), \qquad (9.15)$$

where

$$R_\infty = \frac{2\pi^2 e^4 m}{ch^3}. \qquad (9.14b)$$

(2) **Electronic Orbits for Hydrogen and Ionized Helium:** On the basis of Bohr's model the different energy levels observed spectroscopically for hydrogen (discussed in Section 1) are identified with the series of electronic orbits for which the energy values are determined by equation (9.11). In this case $Z = 1$, and hence the energy corresponding to an orbit of *principal*[1] quantum number n is

$$- W_n = E_n = - Rch/n^2. \qquad (9.16)$$

In the normal state, the electron revolves in a circular orbit of quantum number $n = 1$, while the so-called "excited states" correspond to circular orbits of higher quantum numbers. From equation (9.6) it follows that the diameter of the nth orbit is

$$2a_n = \frac{e^2}{W_n} = \frac{n^2 e^2}{Rch}, \qquad (9.17)$$

and that consequently, as shown in Fig. 9.1, the different orbits are represented by co-planar circles whose radii vary as n^2.

The radius of the orbit corresponding to $n = 1$, as calculated by means of the value $R = R_\infty$, is ordinarily designated by a_0. The value is given by the relation

$$a_0 = \frac{h^2}{4\pi^2 m e^2} = 0.5292 \times 10^{-8} \text{ cm.}$$

The transitions corresponding to three of the spectral series are also shown in Fig. 9.1. From equation (9.16) it follows that the ionization potential of hydrogen (corresponding to $n = 1$) is 13.595 electron volts, while the first resonance potential is

$$V_r = 13.595(1 - \tfrac{1}{2}^2) = 10.20 \text{ volts.}$$

[1] This designation is used because, as shown in subsequent sections, it has been found necessary in discussing more complex spectra to introduce two other quantum numbers.

As mentioned already the value of R should vary, according to Bohr, with the nuclear mass. Consequently corresponding spectral lines for the two isotopes of hydrogen (^{1}H and ^{2}H) should differ slightly in wave length and it was, in fact, by careful spectroscopic measurements of this nature that H. C. Urey, F. G. Brickwedde and G. M. Murphy [1] were led to the discovery of deuterium (^{2}H). Another system for which some of the spectral lines are very close to those observed in the spectrum of hydrogen is that of ionized
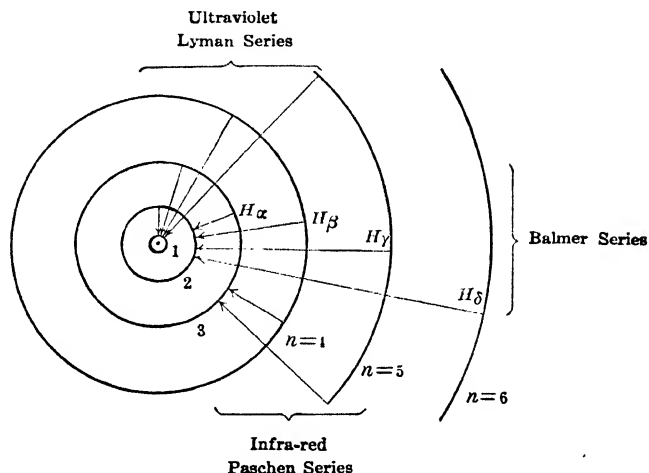
FIG. 9.1. Circular Bohr Orbits for Hydrogen Atom

helium (He$^+$). The atomic masses (on the basis O = 16.000) and values of R for these three systems are as follows:

	Atomic Mass*	Rydberg Constant
^{1}H	1.007857 ± 0.000026	109677.76
^{2}H	2.014186 ± 0.000045	109707.39
He$^+$	4.00281 ± 0.00011	109722.40

In the case of ionized helium, $Z = 2$, and hence the frequency of any line in the spectrum of this ion is given

$$\nu = 4Rc\left(\frac{1}{k^2} - \frac{1}{n^2}\right) = Rc\left\{\frac{1}{(k/2)^2} - \frac{1}{(n/2)^2}\right\}.$$

Accordingly for even values of k and n, lines in this spectrum should lie very close to those observed in the spectrum of hydrogen.

[1] *Phys. Rev.*, **40**, 1, (1932).
* Personal communication from R. T. Birge, Aug. 1939; see also Appendix.

The fact that Bohr was able to account for the slight differences in wave length associated with corresponding lines in the two spectra by means of the difference in values of R must be regarded as another of the important achievments of this theory.[1]

The value of R_∞ as deduced from the values of R obtained spectroscopically for ^1H, ^2H and He^+ is $109,737.45 \pm 0.06$ cm.$^{-1}$. Now, as shown by F. G. Dunnington [2] the relative accuracy of the determinations of R_∞, e and e/m_0 are considerably greater than those of h/e, or of any of the other quantities which involve h. It would therefore appear that these three quantities should lead to a more accurate value for h than the more direct methods based on the application of Einstein's law. This is the method advocated by R. T. Birge.

Assuming the value of R_∞ stated above and the values $e = 4.8022 \times 10^{-10}$ abs. e.s.u., $e/m_0 = 1.7591 \times 10^7$ abs. e.m.u. gm.$^{-1}$ and $c = 2.99776 \times 10^{10}$ cm. sec.$^{-1}$, we obtain the result,

$$h = \left(\frac{2\pi^2}{c} \cdot \frac{e^5}{R_\infty} \cdot \frac{m_0}{e} \right)^{1/3} \tag{9.18}$$

$$= 6.6236 \times 10^{-27} \text{ erg sec.}$$

which is the value adopted in this chapter.

(2) **Principle of Correspondence:** According to Planck's original theory radiation of frequency ν is emitted by an oscillator of the *same* frequency. This is evidently in contradiction with Bohr's hypothesis. According to the latter the frequency of radiation emitted is not identical with the frequency of revolution of the electron in either the initial or final orbit. However, Bohr did attempt to deduce a correlation between these different frequencies and this led to the Principle of Correspondence which has played an important role in the new mechanics as well as in the older quantum mechanics of Bohr and Sommerfeld.

Let us consider in the case of the hydrogen atom the transition between two orbits of quantum numbers n and $n + \Delta n$, where n is a very large number and Δn represents a very small integral increment. The frequency of radiation emitted or absorbed in this transition is given by

$$\nu = Rc \left\{ \frac{1}{n^2} - \frac{1}{(n + \Delta n)^2} \right\}$$

$$= Rc \frac{2\Delta n}{n^3}, \tag{9.19}$$

for n very large compared with Δn.

But from equation (9.10), it is seen that the frequency of revolution of the electron in the nth orbit,

$$\omega_n = \frac{2W_n}{nh} = \frac{2Rc}{n^3}. \tag{9.20}$$

---

[1] For more comprehensive discussion of this topic see Ref. H. E. W., Chap. II.

[2] *Rev. Mod. Phys.*, **11**, 65 (1939).

Therefore,

$$\nu = \omega \cdot \Delta n. \tag{9.21}$$

Hence, it follows that *in the limit, for very large quantum numbers,* and therefore for very low frequencies of revolution of the electron in its orbit, the frequency of radiation emitted or absorbed in a transition for which $\Delta n = 1$, is equal to the frequency of revolution of the electron in its orbit, while for $\Delta n = 2$, the spectroscopic frequency is twice the frequency of revolution, and so forth for $\Delta n = 3$, etc.

Table 9.1[1] gives numerical illustrations of the relationship between the spectroscopic frequency, ν_f, and frequencies of revolution in initial and final states for different values of n.

<div align="center">TABLE 9.1</div>

Initial Quantum No. $n + \Delta n$	Final Quantum No. n	Initial Frequency of Revolution ω'	Spectroscopic Frequency ν_f	Final Frequency of Revolution ω''
2	1	0.82×10^{15} sec.$^{-1}$	2.47×10^{15}	6.58×10^{15}
10	9	6.58×10^{12}	7.72×10^{12}	9.02×10^{12}
30	29	2.44×10^{11}	2.56×10^{11}	2.70×10^{11}
30	28	2.44×10^{11}	$\left\{ \begin{array}{c} 5.41 \times 10^{11} \\ = 2 \times 2.70 \times 10^{11} \end{array} \right\}$	3.00×10^{11}
1000	999	6.58×10^{6}	6.59×10^{6}	6.60×10^{6}

"It is to be observed" Van Vleck remarks, "that in a one quantum transition, the spectroscopic frequency is to be compared with the fundamental revolution frequencies, while in a two quantum leap (illustrated in the next to the last row) the comparison must be made with the octaves or first harmonics $2\omega'$ and $2\omega''$. In a three quantum transition, we would have $3\omega' < \nu < 3\omega''$, etc."

The relations between ω and ν_f illustrated numerically in Table 9.1 may also be represented graphically as emphasized by H. A. Lorentz. Since $W_n = Rch/n^2$, it follows from equation (9.20) that

$$\omega_n = -\frac{1}{h} \cdot \frac{dW_n}{dn} = \frac{1}{h} \cdot \frac{dE_n}{dn}. \tag{9.22}$$

If E_n for the hydrogen atom is plotted against n as abscissa, the points representing the different stationary states are found to lie on a curve such as that shown in Fig. 9.2.[2] Two adjacent levels are represented by E' and E'',

[1] J. H. Van Vleck, "Quantum Principles and Line Spectra," p. 25; *Bull. Nat. Res. Council,* **10**, Pt. 4 (1926).

[2] P. D. Foote, *J. Franklin Inst.,* **198**, 344, 517 (1924). The reader will note the similarity between Fig. 9.1 and Fig. 1.3.

and the frequencies of revolution in the corresponding orbits are denoted by ω' and ω''. According to equation (9.22), the *slope of the curve* at each point,

$$dE/dn = h\omega,$$

and hence is proportional to the corresponding frequency of revolution.

For $\Delta n = 1$, ν_f is obtained from the relation

$$\Delta E = E' - E'' = h\nu_f,$$

that is, from the slope of the line joining the two points, as shown in the figure. It is evident that for *very large values of n* the slope of the secant approaches asymptotically the value of the slope at either point, that is,

$$\nu_f = \omega' = \omega''.$$

Now according to classical theory, as has been stated previously, any periodic motion of an electron or oscillator should give rise to radiation having the same frequency or a combination of this frequency and simple harmonics. Therefore an electron rotating about a nucleus with given frequency ω should radiate energy of the same frequency, and no other. If the motion of the electron is multiply periodic, that is, may be represented as a combination of different frequencies ω_1, ω_2, etc., then the emitted radiation should also contain these frequencies.

The longer wave lengths of radiation are emitted according to Bohr's theory because of transitions between adjacent orbits of large quantum numbers, that is, orbits in which the frequency of revolution of the electron is low. Hence the observation that for such transitions the frequency of radiation emitted approximates more and more to the frequency of revolution of the electron shows that under these conditions the Bohr theory and classical theory tend to give the same results. This is analogous to the observation made in a previous section that for longer wave lengths in black body radiation the Jeans-Rayleigh equation, which is based on classical theory, yields practically the same results as the quantum theoretical expression derived by Planck.

Bohr has stated this conclusion in the form of a generalization which he has designated as the *Principle of Correspondence*. It is merely a statement of the assumption that *in the limit, for very low frequencies of radiation, the results obtained by the quantum theory must be in quantitative agreement with those obtained on the basis of classical theory*. The principal application of this principle by Bohr has been the determination of the correct form of quantum theoretical conclusion for a given problem by comparison with the expectation based on classical theory. In other words, given the answer in terms of the
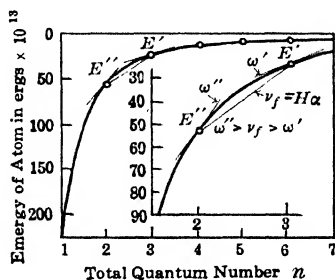

Fig. 9.2. Relation Between Frequency of Revolution (w) and Frequency of Radiation (ν_f), Illustrating Correspondence Principle

classical theory for the case of low frequencies, the form of the quantum theoretical solution is also obtained, since the two solutions must be in agreement in the region of large quantum numbers.

While various applications of this principle will be mentioned in subsequent sections, it is of interest to indicate one such application, viz., to the problem of the hydrogen atom.

As shown above, classical mechanics leads to the relation

$$\omega_n = \sqrt{\frac{2W^3{}_n}{\pi^2 e^4 m}} .$$

(9.8)

But

$$\nu_f = \omega_n = -\frac{1}{h} \cdot \frac{dW_n}{dn} .$$

Hence

$$-\frac{1}{h} \cdot \frac{dW_n}{dn} = \sqrt{\frac{2W_n{}^3}{\pi^2 e^4 m}} .$$

(9.22)

Integrating this equation, and setting the integration constant equal to zero (which is implied in Bohr's postulates), we obtain the result

$$W_n = \frac{2\pi^2 e^4 m}{n^2 h^2} .$$

(9.11)

By comparison with the spectroscopic term value,

$$W_n = Rch/n^2,$$

we obtain the value for R deduced above.

These results were obtained in the previous section by introducing a quantizing condition for the angular momentum in order to determine the discrete values of W. In the above derivation, as will be observed, this assumption is not introduced, but in its place application is made firstly of the observations on the form of spectral series, interpreted by Bohr's postulate of energy levels, and secondly of the Principle of Correspondence.

(3) **Significance of Quantum Condition. Phase Integral:** The assumption introduced by Bohr that the angular momentum of the electron must vary by integral values of $h/2\pi$ for the different discrete states of the atomic system is, in reality, another method of expressing Planck's assumption that the energy of a linear oscillator is always an integral multiple of $h\nu$.
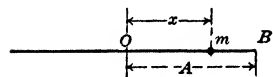
Fig. 9.3. Instantaneous and Maximum Amplitudes of Vibration for Linear Harmonic Oscillator

"In Fig. 9.3 [1] let a particle of mass m vibrate with simple harmonic (linear) motion about a center O with an amplitude A and a frequency ν. The dis-

[1] This discussion and Figs. 9.3 and 9.4 are taken from ref. F. K. R. pp. 363–365.

placement x at any instant is given by

$$x = A \sin 2\pi\nu t, \tag{9.23}$$

where t is the time measured from an instant when the particle is at the center O. The energy E of the system oscillates between all kinetic at O and all potential at maximum displacement. Planck's assumption was that the oscillator could have energy only in multiples of $h\nu$, i.e., that

$$E = nh\nu, \tag{9.24}$$

where n is an integer.

"The total energy of the system is obtained by computing the kinetic energy $E = \frac{1}{2}(mv^2_{max}.)$ at mid-position. Since

$$\left. \begin{array}{l} v = \dfrac{dx}{dt} = 2\pi\nu A \cos 2\pi\nu t \\[2mm] v_{max}. = 2\pi\nu A. \end{array} \right\}$$

and

Therefore

$$E = \tfrac{1}{2}mv^2_{max}. = 2\pi^2\nu^2 A^2 m. \tag{9.25}$$

"As the particle oscillates, its momentum p_x changes from zero at maximum displacement B to a maximum at midpoint O. The momentum at any point in the path is given by

$$p_x = m \frac{dx}{dt} = 2\pi\nu A m \cos 2\pi\nu t. \tag{9.26}$$

"Now, plot a curve (Fig. 9.4) with p_x as ordinates and the displacement x as abscissae. The figure can readily be shown to be an ellipse. The area, S, of the figure is obviously given by

$$S = \int p_x dx, \tag{9.27}$$

taken over the complete cycle. Since

$$dx = 2\pi\nu A (\cos 2\pi\nu t) dt,$$

Fig. 9.4. Relation Between Momentum and Displacement for Linear Oscillator

we have, using equations (9.26) and (9.27),

$$S = 4\pi^2\nu^2 m A^2 \int_{t=0}^{t=1/\nu} \cos^2 (2\pi\nu t) dt.$$
$$= 2\pi^2\nu m A^2.$$

If we write this equation in the form

$$S = \frac{2\pi^2\nu^2 m A^2}{\nu}, \tag{9.28}$$

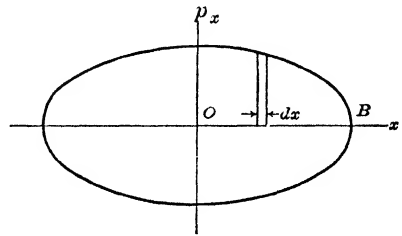and combine with equations (9.25) and (9.24), we can write the last equation in the form

$$S = \oint p_x dx = \frac{nh\nu}{\nu} = nh, \tag{9.29}$$

where $\oint$ means *'integration over a complete cycle.'*

"That is to say: *On the basis of Planck's hypothesis, as given by equation (9.24), the integral $\int p_x dx$, taken over a complete cycle, can take on only a series of values obtained by multiplying the universal constant h by the integers* 0, 1, 2, 3, $\cdots$. In terms of Fig. 9.4, this means that out of an infinite number of ellipses *geometrically* possible, we have a limited number; one ellipse for $n = 1$, another for $n = 2$, another for $n = 3$, etc. The area *between* successive ellipses is numerically equal to h. The integral in equation (9.29) is spoken of as the *phase integral*. We may assume, however, in accordance with the heuristic methods of applying the quantum conditions, that an equation of this type is generally applicable whenever with any coordinate q (corresponding to x) there is associated a momentum p (corresponding to p_x), so that, in general, we may apply to the coordinate q and the corresponding momentum p the integral

$$\oint p dq = nh.\text{"} \tag{9.30}$$

In fact, this very important conclusion, which was derived independently by Wilson and Sommerfeld, may be derived from the Principle of Least Action in ordinary mechanics, which, as mentioned previously, states that for any (conservative) dynamical system, with constant energy, the value of $\int p dq$ taken between the initial and final points on the path is a minimum (and therefore constant). The integral defines the "change in Action." Hence, for a periodic type of motion, $\oint p dq$ should also be a constant; and therefore the assumption made in the quantum theory is that this integral has the value nh, since h also has the same dimensions as the product pq.

From equation (9.28) above it also follows that this integral can be expressed in the form

$$\int_0^{1/\nu} 2T dt = nh, \tag{9.31}$$

where T is the kinetic energy at any instant. This equation also follows from the more general relations,

$$\int_0^{1/\nu} 2T dt = \int_0^{1/\nu} mv \cdot v dt = \oint p dq. \tag{9.32}$$

For an electron revolving in a circular orbit, the kinetic energy is constant, since the orbital velocity is constant. Hence, in accordance with Planck's condition

$$\int_0^{1/\nu} 2T dt = \frac{mv^2}{\omega} = nh.$$

That is,

$$mv \cdot v/\omega = nh.$$

But

$$v = 2\pi a\omega.$$

Therefore

$$mva = \frac{nh}{2\pi},$$

which is Bohr's statement of the quantum condition for this case.

The quantizing condition expressed in (9.29) may be extended to systems possessing more than one frequency of motion (or degree of freedom), and if these frequencies are independent (conditionally periodic systems), then it is postulated that for each of these types of motion, we must have

$$\oint p_i dq_i = n_i h, \tag{9.33}$$

where n_i may be a different integer (not necessarily so) for each of the different types of motion.

(4) **Elliptic Orbit–Azimuthal Quantum Number:** In Section 1 brief mention was made of the fact that in the case of sodium and other metals of the alkali metal group there are four series of terms, which were designated formerly as s, p, d and f. It was found that the wave numbers of spectral lines for each of these series could be represented by a relation, similar to Balmer's, of the form,

$$\tilde{\nu}_m = \tilde{\nu}_\infty - \frac{R}{(m + \alpha)^2}, \tag{1.9}$$

where the value of R is approximately the same as that of R_∞ or R_H while α is a constant for any one series and m is the number of the term in the series. Thus $\tilde{\nu}_\infty$ corresponds to the value of $\tilde{\nu}_m$ for $m = \infty$ and represents the limit of the series. As will be observed from the expressions for the spectral lines in the different series, the *diffuse* and *sharp* series have the same limit, $\tilde{\nu}_\infty = R/(2 + p)^2$, which is the first member of the principal series. The limit of the latter is the first member of the sharp series, while the limit of the fundamental series is the first member of the d-series of terms.

Table 9.2 gives the values of λ, $\tilde{\nu}$ and m [1] for a few of the lines of the principal series. The column under mp gives the values of the corresponding terms, derived by the relation,

$$(mp) = \frac{R}{(m + p)^2} = \frac{R}{(1 + s)^2} - \frac{1}{\lambda}. \tag{9.34}$$

It will be observed that the limit of this series is $\tilde{\nu} = 41,449$. The column under n gives the values of the principal *quantum numbers* for these terms as

---

[1] This use of the letter m should not be confused with the symbol for the mass of the electron.

TABLE 9.2 *

λ	$\tilde{\nu}$	m	(mp)	n	$n_{\text{eff.}}$	α_k
5890	16973	2	24476	3	2.127	0.873
3302	30271	3	11177	4	3.148	.852
2853	35043	4	6406	5	4.158	.842
2680	37298	5	4151	6	5.164	.836
2464	40565	11	883	12	11.19	.81
2426	41203	21	245	22	21.25	.75
2418	41342	32	106	33		
2413	41449	∞	0			

* This table really gives only the mp_1 lines and terms of the series. As mentioned in Section 1 and shown in Fig. 1.5 there are actually two sets of terms, mp_1 and mp_2 (designated now as $m^2P_{3/2}$ and $m^2P_{1/2}$ respectively) which lie very close to each other. Furthermore, although the values of λ, $\tilde{\nu}$, etc., have been determined to a much higher degree of accuracy, the nearest integral values only are given in the table. For further details on the accurate values of the terms and wave-numbers of lines, the reader is referred to the following publications.

A. Fowler, "Report on Series in Line Spectra," London (1922) and F. Paschen and R. Götze, "Seriengesetze der Linienspektren," Berlin (1922).

determined from considerations based on the electronic configuration of the sodium atom; $n_{\text{eff.}}$ is the value of the effective quantum number, derived from the relation

$$n_{\text{eff.}} = \sqrt{\frac{R}{\tilde{\nu}}} = \sqrt{R\lambda} \qquad (9.35)$$

while α_k $(= n - n_{\text{eff.}})$ is known as the "quantum defect." The significance of the values in the last two columns is discussed below.

In accordance with Bohr's point of view, the four series of terms must correspond to four different sets of energy levels in the atomic system, and Fig. 1.5 shows these levels for sodium, arranged in columns, with the transitions between them, which give rise to the observed spectral lines. As mentioned previously, the p, d, and f series are actually of the doublet type and according to present notation, the p-series are designated $^2P_{1/2}$ and $^2P_{3/2}$, the d-series as $^2D_{3/2}$ and $^2D_{5/2}$, and the f-series as $^2F_{5/2}$ and $^2F_{7/2}$. The question thus arises regarding the interpretation of two kinds of observations: firstly, those on the occurrence of terms of types S, P, D, F, etc., and secondly, those on the occurrence of doublet terms in the case of alkali metals, of triplets and singlets in the case of elements of group II, and of still higher degrees of multiplicity for elements in the other groups in the Periodic Arrangement. In the present section we shall consider the first of these questions, leaving the discussion of the second question for a subsequent section.

It became evident, very soon after Bohr enunciated his theory of the origin of spectral lines that the simple theory devised for the hydrogen atom could not be used to explain these other observations. The atom-model which was gradually developed during the period 1916–1925, and which was based largely

on the suggestions of Sommerfeld, Landé, Hund and others, offered a fairly satisfactory qualitative representation of the spectroscopic facts and served an extremely useful purpose in correlating an immense number of observations. However, the model finally became rather "top-heavy," as it were; it could not be brought into agreement with the laws of ordinary mechanics, and inconsistencies developed. Hence arose the necessity for a fundamentally new point of view and the consequent evolution of a new mechanics of atomic structure.[1]

In the theory of the simple hydrogen atom discussed above, the electronic orbits were regarded as circular. However, in the general case of motion under the action of a central force varying inversely as the square of the distance, the path is an ellipse with the central (much larger) body at one of the foci. While the complete discussion of the motion is reserved for a subsequent section, only those conclusions will be mentioned which are of importance in the interpretation of spectroscopic terms.

In Fig. 9.5 let the path of the electron be the ellipse of semi-major axis, a, and semi-minor axis, b. The eccentricity, ϵ, is defined as the ratio c/a where c is the distance from center of ellipse to one of the foci. The motion is best described in terms of the polar coördinates: the radius vector, r, and ϕ, the angle described by the radius

Fɪɢ. 9.5.   Illustrating Elliptic Orbit of Electron

vector. The tangential velocity v at any point has as components: the radial velocity $dr/dt \equiv \dot{r}$, and a component at right angles to this, equal to $rd\phi/dt \equiv r\dot{\phi}$. The corresponding components of momentum are

$$p_r = m\dot{r},$$
$$p_\phi = mr^2\dot{\phi}.$$

where m = mass of electron.

From Kepler's second law of motion (radius vector describes equal areas in equal intervals of time) it follows that p_ϕ = constant.

Now Sommerfeld applies to *each* of these momenta the quantum condition for the phase integral, equation (9.33). Consequently,

$$\oint p_\phi d\phi = kh,$$
$$\oint p_r dr = n_r h,$$

where k is an angular or *azimuthal* quantum number, and n_r is a *radial* quantum number.

[1] For further details the reader should consult the following: K. K. Darrow, Introduction to Contemporary Physics, D. Van Nostrand Company, New York (1926); A. Sommerfeld, Atombau und Spektrallinien, 4th ed., Vieweg und Sohn, Braunschweig (1924); F. Hund, Linienspektren und periodisches System der Elemente, Julius Springer, Berlin (1927); J. H. Van Vleck, *loc. cit.*
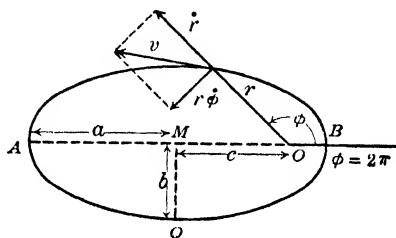
The state of the atom is defined by a total quantum number, $n = k + n_r$, the number n being identical with the quantum number previously used for defining the state of the atom with circular orbits.

Now, writing the equation for the ellipse in terms of r and ϕ, it is possible to evaluate the two phase integrals,[1] and it can be shown that

$$1 - \epsilon^2 = k^2/n^2, \tag{9.36}$$

and

$$E = - \frac{Ze^2}{2a} \tag{9.37}$$

$$= - \frac{2\pi^2 m Z^2 e^4}{h^2(k + n_r)^2} = \frac{2\pi^2 m Z^2 e^4}{h^2 n^2}$$

$$= - \frac{RchZ^2}{n^2}, \tag{9.38}$$

while the frequency of revolution is given by

$$\frac{1}{\omega^2} = \frac{4\pi^2 m a^3}{Ze^2}. \tag{9.39}$$

This is merely a statement of Kepler's third law of motion that the square of the period of revolution varies as the cube of the major axis of the elliptic orbit. From (9.37) and (9.38) it follows that

$$2a = n^2 \frac{h^2}{2\pi^2 Z e^2 m} \tag{9.40}$$

and from (9.36) it may be deduced that

$$\frac{b}{a} = \frac{k}{n}. \tag{9.41}$$

Equation (9.37) shows that the energy of the atom is dependent only upon the value of the major axis and therefore independent of the eccentricity, and from (9.38) it follows that, as in the case of the circular orbit, the energy is expressed in terms of a single quantum number, n. Apparently there is no gain in introducing a second quantum number, k.

However, *this conclusion is valid only if the electron revolves in a simple Coulomb field.* If, on the other hand, the attractive force acting on the electron is not constant for different points on its orbit, the motion can no longer be described as a simple elliptic orbit, but becomes more complex. This is the case when the number of electrons in the atomic system is greater than one. For then we must take into account the fact that the particular electron

---

[1] See A. Sommerfeld, Atombau und Spektrallinien, 4th edition, Vieweg & Sohn, Braunschweig (1924), p. 122, *et seq.*

whose transitions we are considering is acted upon not only by the nucleus, but also by all the other electrons external to the nucleus.   This electron, which is effective in producing the radiation, corresponds ordinarily to one of the valence electrons, and it has been designated by German writers as the "Leuchtelektron."

Now, in the normal state, this electron as it travels in its orbit will pass very close to the nucleus at one point on its path (perihelion position) and will there be acted upon by an *effective charge Z*, which is the difference between the charge on the nucleus and the negative charge on the electrons which are located between the leuchtelektron and the nucleus.   On the other hand, if the orbit is very eccentric, then the effective charge acting on this electron when it is farthest from the nucleus (aphelion position) will be practically $Z = 1$, since all the other electrons will act as a screen between nucleus and leuchtelektron.

Under these conditions the force acting on the electron may be regarded as constituted of a *Coulomb field of force upon which is superimposed a perturbing central force.*   In consequence of this, the orbit will no longer be simply periodic, that is, characterized by one frequency, ω_1. Owing to the perturbing action of the extra field there will occur, as may be deduced from dynamical considerations, a uniform precession in the orbital plane, the precessional frequency being represented by ω_2, and the path of the electron will have the form of a rosette as shown in Fig. 9.6.   The value of ω_2 will obviously vary with the eccentricity of the ellipse and therefore it will be expected that different elliptic orbits having the same value of the major axis, and therefore the same quantum number n, will necessarily possess different values of the total energy because of the different frequencies of precession.
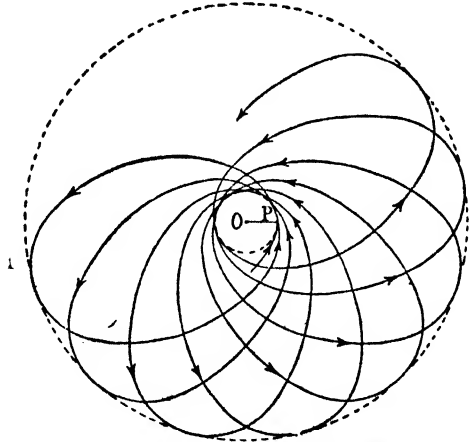

Fig. 9.6.   Rosette Showing Precession of Elliptic Orbit

On the basis of the Correspondence Principle, it follows that the frequencies ω_1 and ω_2 will be related to the total energy by relations of the form

$$\omega_1 = \frac{1}{h} \cdot \frac{\partial E}{\partial n},$$

$$\omega_2 = \frac{1}{h} \cdot \frac{\partial E}{\partial k}.$$

That is, E is a function of *both* n and k, and therefore the frequency of light

produced will be given by a relation of the form

$$h\nu = E(n_1, k_1) - E(n_2, k_2)$$

where $E(n, k)$ denotes the energy in each state as dependent upon the values of n and k.

Value of n	k	l	Major Axis	Minor Axis
1	1	0	a	a
2	2	1	$4a$	$4a$
	1	0		$2a$
3	3	2	$9a$	$9a$
	2	1		$6a$
	1	0		$3a$
4	4	3	$16a$	$16a$
	3	2		$12a$
	2	1		$8a$
	1	0		$4a$

According to equations (9.36) and (9.41), the eccentricity and ratio of minor to major axis of the elliptic orbits can assume only those values which are given by integral values of k and n. Furthermore, it is evident that the minimum value of k is 1 (for an orbit of large eccentricity), while the maximum value is $k = n$ (a circular orbit). Thus, corresponding to different values of n, there will be the values of k (or $l = k - 1$) given in the above table.

The different orbits in relation to the nucleus are illustrated in Fig. 9.7, a_0 designating the radius of the normal orbit in the H atom. From equation (9.41) it follows that the smaller the value of k for given values of n, the nearer the electron will approach the nucleus at perihelion. It would therefore be expected that the perturbing effect of electrons revolving in orbits very close to the nucleus will be greatest for orbits for which $k = 1$, and least for orbits for which $k = n$.

FIG. 9.7. Bohr-Sommerfeld Orbits for Different Values of n and k with Corresponding Spectral Types of Terms and Assignment of Quantum Number l on Basis of Wave Mechanics

We thus arrive at a distinction pointed out by Bohr between *non-penetrating* or hydrogen-like, and *penetrating orbits*. As an illustration of the application

of these ideas, we shall consider the normal orbit of the valence electron in sodium for which, as will be shown below, $n = 3$, $k = 1$. The atom has a nuclear charge of 11, and therefore has 11 electrons revolving around the nucleus. If we consider the structure of the ionized atom (Na^+) the electron configuration resembles that of neon, which has ten electrons. "As shown by X-ray data, two of these electrons are bound closely to the nucleus, in a configuration resembling helium, and the other eight revolve in larger orbits. Data from many sources suggest that these eight outer electrons pair off symmetrically as far as their effects a short distance from the atom are concerned, so that the field just outside the neutral neon atom decreases inversely as a high power of the distance. Accordingly the field just outside the sodium ion is practically equivalent to that of a unit nuclear charge ($Z = 1$). For purposes of rough computation we may therefore represent the sodium atom with the valence electron in its normal orbit in the following manner. The two innermost electrons partially neutralize the nuclear charge, leaving a net nuclear charge of $+ 9$. This is surrounded by a rigid shell of negative charge representing the eight outer electrons of the kernel (residue of atom after removal of valence electron). The normal orbit penetrates this shell as illustrated in Fig. 9.8. Outside the shell the valence electron is acted upon by unit positive charge, and the field is strictly of the Coulomb or hydrogen type. After the electron penetrates the shell, it is subjected to a Coulomb field due to a positive charge of nine units. Such orbits are mathematically calculable and have the general form illustrated.

Fig. 9.8. Penetration of Inner "Shell" of Electrons by Valence Electron in Sodium

The complete orbit consists of a series of outer and inner loops, each loop being elliptical. Precession of the orbit occurs entirely within the uniform shell of charge." [1]
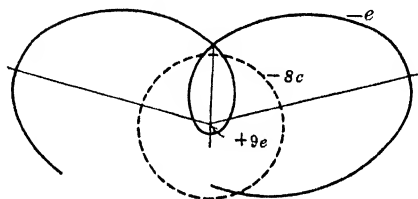
It is evident that for the same value of n, the value of W will increase with decrease in k, owing to increase in the effective value of Z, and the increased binding of the electron. It is therefore on the basis of such considerations that the different series in sodium and allied elements have been assigned different values of k, or (l), as shown in the following table:

Series of Terms	Designation	k	l
Sharp................................	S	1	0
Principal............................	P	2	1
Diffuse..............................	D	3	2
Fundamental........................	F	4	3

[1] This quotation and Fig. 9.8 are taken from the paper by P. D. Foote, *J. Franklin Inst.*, **198**, 344, 517 (1924).

The last column of the table gives the value of $l = k - 1$, the subsidiary quantum number which is used in the new mechanics, instead of k. We may now proceed to show that this assignment of k- (or l-) values to the different types of terms is in accord with deductions from the actual values of the terms.

Mention has been made previously of the Rydberg formula, $R/(m + a)^2$, for terms in the arc spectra of the alkali elements. The values of m assigned in accordance with this relation by spectroscopists are less than the values of the principal quantum number, n, which it has been found necessary to assign to these terms in accordance with the conclusions on the electronic configurations in atoms. The reason for this is evident from the following considerations.
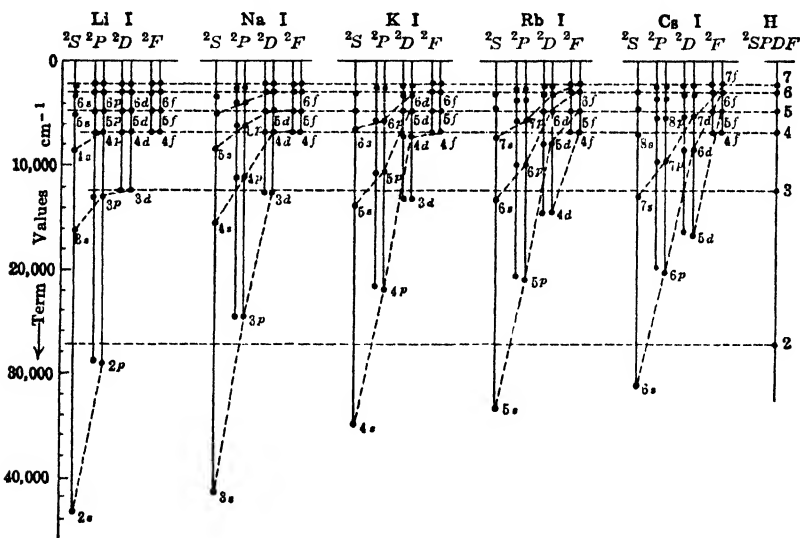
FIG. 9.9.   Energy Levels in Spectra of Alkali Metals Compared with Those of Hydrogen

Let n denote the real quantum number and $Z_{\text{eff.}}$ the effective value of the charge acting on the electron. Then, to a first approximation

$$W = \frac{RchZ_{\text{eff.}}^2}{n^2}.$$ (9.42)

or $\tilde{\nu} = RZ_{\text{eff.}}^2/n^2$. It is, however, much more convenient to consider that for both types of orbits $Z = 1$ when we are dealing with arc spectra. Hence, since W or $\tilde{\nu}$ has a perfectly definite value, we must write

$$\tilde{\nu} = \frac{R}{(n - \alpha_k)^2} = \frac{R}{n_{\text{eff.}}^2}.$$ (9.43)

That is, a calculation of $n_{\text{eff.}}$ from the value of $\tilde{\nu}$ gives a value which is less than n by the amount α_k, the latter being known as the "quantum defect."

If now we calculate the values of n_{eff} and α_k for the lowest terms in the four spectral series of the alkali metals, and compare these values with those of n as derived from considerations of electronic distribution, we obtain the results shown in Table 9.3. The values of n_{eff} were derived from the spectroscopically measured wave numbers of the terms by the relation

$$n_{eff.} = \sqrt{109{,}722/\bar{\nu}}.$$

It will be observed that the values of the quantum defects decrease as we pass from S to F terms, i.e., as k (or l) increases. Now from the foregoing considerations it is evident that a D-term ($k = 3$) will occur for the first time for a term having $n = 3$. This will correspond to an approximately circular orbit, of the non-penetrating type. We would therefore expect that for such an orbit the value of n_{eff} would be approximately the same as that of n. Similarly the first F-term will appear for $n = 4$, and this will correspond to a non-penetrating orbit, so that for this term n_{eff} is practically equal to n. On the other hand, for a term having the quantum numbers $n = 4$, $k = 1$, corresponding to a penetrating orbit of high eccentricity, the value of α_k should be very large, as is seen from a comparison of the values for S and F terms for potassium.

TABLE 9.3

Atom		S	P	D	F
H	n	1.00	2.00	3.00	4.00
	n	2.00	2.00	3.00	4.00
Li	$n_{eff.}$	1.59	1.96	3.00	4.00
	α_k	0.41	0.04	0.00	0.00
	n	3.00	3.00	3.00	4.00
Na	$n_{eff.}$	1.63	2.12	2.99	4.00
	α_k	1.37	0.88	0.01	0.00
	n	4.00	4.00	3.00	4.00
K	$n_{eff.}$	1.77	2.23	2.85	3.99
	α_k	2.23	1.77	0.15	0.01
	n	5.00	5.00	3.00	4.00
Rb	$n_{eff.}$	1.80	2.28	2.77	3.99
	α_k	3.20	2.72	0.23	0.01
	n	6.00	6.00	3.00	4.00
Cs	$n_{eff.}$	1.87	2.33	2.55	3.98
	α_k	4.13	3.67	0.45	0.02

It was such observations, on the values of α_k for different terms, which led Bohr to the correlation of orbital type and value of k. Fig. 9.9 [1] shows graph-

[1] Ref. H. E. W., p. 87.

ically the various terms (expressed in wave numbers) in the spectra of the alkali metals compared with those for H. The numbers attached to each term give the corresponding value of n, while the value of n_{eff} may be obtained from that value of n for H which corresponds to the same value of the wave number, $\bar{\nu}$. These are shown in the last column of Fig. 9.9 and correspond to the values of m in Fig. 1.4.

The values of n for the normal orbit of the valence electron (lowest energy level) increase by unity as we pass from the elements of low atomic number to those of higher. The reasons for assigning these values to the particular atoms are based partly on spectroscopic data such as those discussed above, but to an even greater extent on X-ray data, which will be discussed in a subsequent section.

10. The Wave Mechanics Treatment of the Hydrogen Atom [1]

(1) **Solution of the Schroedinger Equation:** As mentioned in Section 8, the Schroedinger equation for a system of three degrees of freedom is of the form

$$\nabla^2\phi + \frac{8\pi^2 m}{h^2}(E - V)\phi = 0, \tag{10.1}$$

where ∇^2 designates the Laplacian operator.

In the case of the hydrogen atom, the potential energy function is given, according to equation (9.5), by the relation

$$V = -\frac{Ze^2}{r} \tag{10.2}$$

where r is the radial distance from the nucleus to the electron. Because V is a function only of r, it is most convenient, in solving equation (10.1), to express the Laplacian operator in terms of the spherical polar coordinates, r, θ, and η, where θ is the angle between the axis of the sphere and the radius vector (corresponding to $\pi/2 -$ "latitude"), and η is the angle between the meridian plane in which r is measured and a fixed meridian plane. Thus η corresponds to the "longitude."

In terms of these coordinates the Schroedinger equation assumes the form:

$$\frac{1}{r^2\sin\theta}\left\{\frac{\partial}{\partial r}\left(r^2\sin\theta\frac{\partial\phi}{\partial r}\right) + \frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\phi}{\partial\eta}\right) + \frac{\partial}{\partial\eta}\left(\frac{1}{\sin\theta}\cdot\frac{\partial\phi}{\partial\eta}\right)\right\}$$
$$+ \frac{8\pi^2 m}{h^2}\left(E + \frac{Ze^2}{r}\right)\phi = 0. \quad (10.3)$$

The boundary conditions which the solution $\phi = \phi(r, \theta, \eta)$ must satisfy

---

[1] For more detailed treatment the reader should consult Introduction to Quantum Mechanics, by L. Pauling and E. B. Wilson, McGraw-Hill Book Company, New York (1935), (Ref. P. W.), or ref. S. D.

are evidently the following:

(1) ϕ must be periodic in θ with period π, and in η, with period 2π.
(2) ϕ must be a continuous and single-valued function of r, which vanishes asymptotically for large values of r, and also for $r = 0$. This is in accord with the "common-sense" notion that the probability of occurrence of the electron per unit volume must decrease to zero for large values of r and also at the origin, where the nucleus is located.

It is found that solutions satisfying these requirements are obtained only for the *same series of discrete values of E* as those deduced by the Bohr theory. That is, the energy states are determined by the relation

$$E_n = -\frac{2\pi^2 me^4 Z^2}{h^2 n^2} = -\frac{RhcZ^2}{n^2} = -\frac{Z^2 e^2}{2n^2 a_0}, \qquad (10.4)$$

where n is a whole number, $R = R_\infty(1 + m/M)$ as stated in the previous section, and a_0 is the radius of the normal Bohr orbit.

Comparing the method used by Bohr for deriving the values of E, with that used by Schroedinger, it would appear at first glance that nothing has been gained by the latter. However, the results obtained by the two methods are the same only in the case of the one-electron system, such as the hydrogen-like atom. In the case of atomic systems such as those of helium, lithium and so forth, where the number of electrons is two or more, it was found impossible, in spite of many attempts by some of the best theoretical physicists, to deduce by application of the Bohr method values of the energy states in agreement with those observed spectroscopically. On the other hand, this has been accomplished by the methods of the new mechanics.

It is also evident that inherently the logic of the Schroedinger equation is simpler (even though the mathematical technique may be more difficult) since it involves only one assumption—that the different energy states correspond to different stationary wave patterns in much the same manner as the different frequencies emitted by a vibrating string are determined by the boundary conditions.

The eigenfunctions associated with the eigenvalues, E_n, may be represented as the product of three functions of the form

$$\phi_{nlm}(r, \theta, \eta) = S_{nl}(r) X_{lm}(\theta) Z_m(\eta), \qquad (10.5)$$

where n, l, and m indicate three quantum numbers which are defined as follows: n is the *total quantum number*; l, which corresponds to $k - 1$ of the Bohr theory and is designated the *azimuthal quantum number*, may have any one of the series of values, $l = n - 1$, $n - 2$, $\cdots$ 0; while m, designated the *magnetic quantum number*, is determined by the relation, $m = \pm l, \pm (l - 1), \cdots 0$.

Thus corresponding to $n = 1$, the normal or lowest state of the hydrogen-like atom, the eigenvalue is $E_1 = -Z^2 e^2/2a_0$, and the eigenfunction has the

form

$$\phi_{100} = -\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-(Zr/a_0)}. \qquad (10.6)$$

Since this function is the same for all values of θ and η it is spherically symmetrical. The radial function, designated in equation (10.5) by $S_{nl}(r)$ is exponential, indicating that ϕ_{100} decreases rapidly with increase in r.

For $n = 2$, there are *four* eigenfunctions, which are as follows:

$$l = 0;\ m = 0;\quad \phi_{200} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(\frac{Zr}{a_0} - 2\right)e^{-(Zr/2a_0)}, \qquad (10.7)$$

$$l = 1;\ m = 0;\quad \phi_{210} = -\frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{5/2} r\cos\theta\, e^{-(Zr/2a_0)}, \qquad (10.8)$$

$$l = 1;\ m = \pm 1;\ \phi_{211} = -\frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{5/2} r\sin\theta\, e^{-(Zr/2a_0)}\, e^{\pm i\eta}. \qquad (10.9)$$

Since these four eigenfunctions are associated with the *same* eigenvalue

$$E_2 = -\frac{Z^2 e^2}{2\times 4a_0},$$

this is known as a *degenerate* state. For any given value of l there are $2l + 1$ functions, corresponding to the values $m = l, l - 1, \cdots, 0, \cdots, -(l - 1), -l$, and for a given value of n, there are n values of l. Hence the total number of eigenfunctions associated with a given value of n is readily found to be n^2, and this defines the *degree of degeneracy for quantum number n*. Thus, for $n = 3$, there are nine eigenfunctions, distributed thus: one s-function, three p-functions, and five d-functions.

The corresponding spectroscopic designations for the lower states of the hydrogen-like atom are as follows·

Spectral designation	n	l	m
1s	1	0	0
2s	2	0	0
2p	2	1	0
	2	1	± 1
3s	3	0	0
3p	3	1	0
	3	1	± 1
3d	3	2	0
	3	2	± 1
	3	2	± 2

In the case of an atomic system with a single valence electron the s-eigenfunctions are associated with the spectroscopic S-terms (discussed in Section 1),

and similar relations exist between p-eigenfunctions and P-terms and d-eigenfunctions and D-terms, respectively.

Figure 10.1 [1] shows plots of the radial eigenfunctions, $S_{nl}(r)$, for $n = 1$, 2, and 3. As ordinates are plotted values of $-S_{nl}(r)Z^{-3/2}10^{-12}$, while the abscissae give values of r/a_0. It will be observed that the number of *nodes* (excluding that at $r = 0$) along the coordinate $\rho = r/a_0$ is equal to $n - (l + 1) = j$. Hence j is designated as the *radial quantum number*
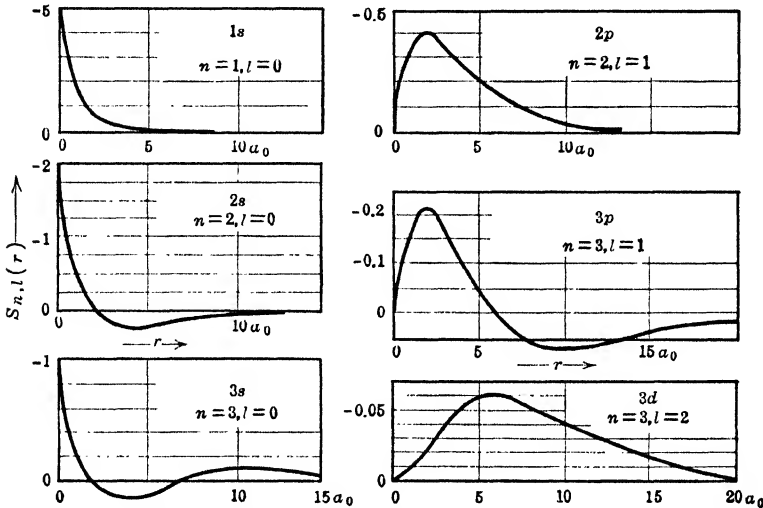
Fig. 10.1.   Plots of Radial Eigenfunctions for Different Electronic States of Hydrogen Atom

Thus quantum numbers appear in wave mechanics for just the same reason as nodal numbers in the case of vibrating systems. For instance, in the case of a string fastened at both ends, the number of nodes is $n - 1$, where n is the order of the emitted harmonic. Similarly in the case of a vibrating two-dimensional system there are two sets of nodal numbers. These numbers will correspond to nodes along the x- and y-axes for a rectangular plate, while a circular plate has one set of nodes with respect to r, the radius vector, and another set which designates the number of nodes with respect to the angle θ.

Whereas in the classical Bohr theory the quantum condition was introduced, for the purpose of determining the discrete orbits, in the form

$$\oint p_i dq_i = n_i h, \tag{9.33}$$

where p_i and q_i are so-called canonically conjugated variables and n_i is a whole number, these quantum numbers occur naturally in wave mechanics as a result of solving the Schroedinger equation.

[1] Ref. H. E. W., p. 67.

The spherical eigenfunctions for $l = 0$ and $l = 1$ are shown in Table 10.1.

TABLE 10.1
NORMALIZED SPHERICAL EIGENFUNCTIONS

Notation	l	m	$X_{l,m}(\theta)$	$Z_m(\eta)$	$X(\theta)Z(\eta)$
s	0	0	$1/\sqrt{2}$	$1/\sqrt{2\pi}$	$1/\sqrt{4\pi}$
p_z	1	0	$\sqrt{3/2}\,\cos\theta$	$1/\sqrt{2\pi}$	$\sqrt{3/4\pi}\,\cos\theta$
p_x	1	$+1$	$\sqrt{3/2}\,\sin\theta$	$(1/\sqrt{\pi})\cos\eta$	$\sqrt{3/4\pi}\,\sin\theta\,\cos\eta$
p_y	1	-1	$\sqrt{3/2}\,\sin\theta$	$(1/\sqrt{\pi})\sin\eta$	$\sqrt{3/4\pi}\,\sin\theta\,\sin\eta$

The first column gives the notation used by L. Pauling for the three p-functions and Fig. 10.2 shows plots of the s and p_x functions. The three p-functions are similar in form, but oriented at right angles to each other with their axes along each of the three coordinate axes.

$s = 1$ $p_x = \sqrt{3}\,\sin\theta\,\cos\eta$
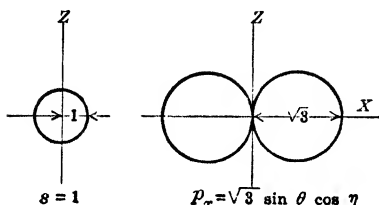
FIG. 10.2. S and p_x Eigenfunctions

(2) **Distribution Functions for Occurrence of Electron:** As pointed out in the Section (8.4), the "amplitude" function ϕ, obtained by solving a particular Schroedinger equation, has no physical significance. But $\bar{\phi}\phi$ or ϕ^2 (if the function is real) is interpreted as the probability of occurrence per unit volume (or unit area, or unit length) at a given point.

In the case of the eigenfunctions $\phi_{nlm}(r, \theta, \eta)$ obtained by solving the partial differential equation for the hydrogen-like atom, the expression

$$\bar{\phi}\phi dv = S^2(r)\ X^2(\theta)\ Z^2(\eta)r^2\sin\theta dr d\theta d\eta, \qquad (10.10)$$

is interpreted as the probability of occurrence of the electron in the element of volume $dv = r^2\sin\theta dr d\theta d\eta$, at the point whose coordinates are r, θ, and η.

Since $Z(\eta)\bar{Z}(\eta) = 1/(2\pi)$, it is seen that the function $\bar{\phi}\phi$ is independent of η. Hence,

$$Pd\theta = \frac{X^2(\theta)d\theta}{2\pi} \qquad (10.11)$$

is the probability of occurrence of the electron in the zone located between θ and $\theta + d\theta$. Fig. 10.3, taken from the treatise by H. E. White [1] shows plots of the function P for different electronic states of the hydrogen-like atom. Instead of regarding P as a probability function it is more convenient to interpret it as *charge distribution function*. In the case $n = 1$, $l = 0$, P is spherically symmetrical, but for $n = 2$, $l = 1$, there are three possible eigen-

[1] *Op. cit.*, p. 63.

functions, as shown in Table 10.1, and hence there are three charge distribution functions as shown at the top of Fig. 10.3.

The description by H. E. White of the different plots shown in this figure is as follows:

"Each curve is shown plotted symmetrically on each side of the vertical axis in order to represent a cross section of the three-dimensional plot. Three dimensional curves are obtained by rotating each figure about its vertical axis. It should be pointed out that the electron is not confined to the shaded areas in each figure. The magnitude of a straight line joining the center and any point on a given curve is a measure of the electron's probability of being found in the direction of that line.

"These figures indicate that for all $m = 0$ states, with the exception of s-electrons, the charge density is greatest in the direction of the poles, i.e., in the direction $\theta = 0$ and π. The exponent of $e^{im\eta}$ being zero implies that there is no motion in the η-coordinate and that the motion of the electron, i.e., the plane of the orbit, is in some one meridian plane through the η-axis, all meridian planes being equally probable."
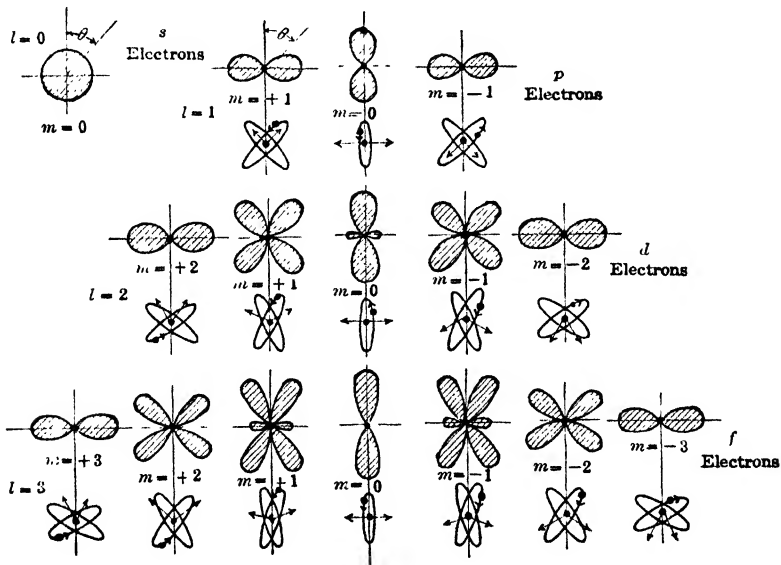
FIG. 10.3. Angular Distribution Functions for Different Electronic States of Hydrogen Atom.

In Fig. 10.3, "the classical oriented orbit for each state is given below each figure, tilted slightly out of the normal plane to show an orbit rather than a straight line."

Let us now consider the radial function, $S_{nl}(r)$. In wave mechanics the function $\{S_{nl}(r)\}^2$ is interpreted as the probability of occurrence of the electron

(or charge density) per unit length at the point defined by the value of r. However, a much better interpretation of this function is obtained by means of the *distribution function*, D, defined by the relation

$$D \cdot dr = 4\pi r^2 \{S(r)\}^2 dr, \qquad (10.12)$$

which gives the *probability of occurrence of the electron* in the *spherical shell located between r and $r + dr$.* Fig. 10.4 taken from the treatise by H. E. White,[1]
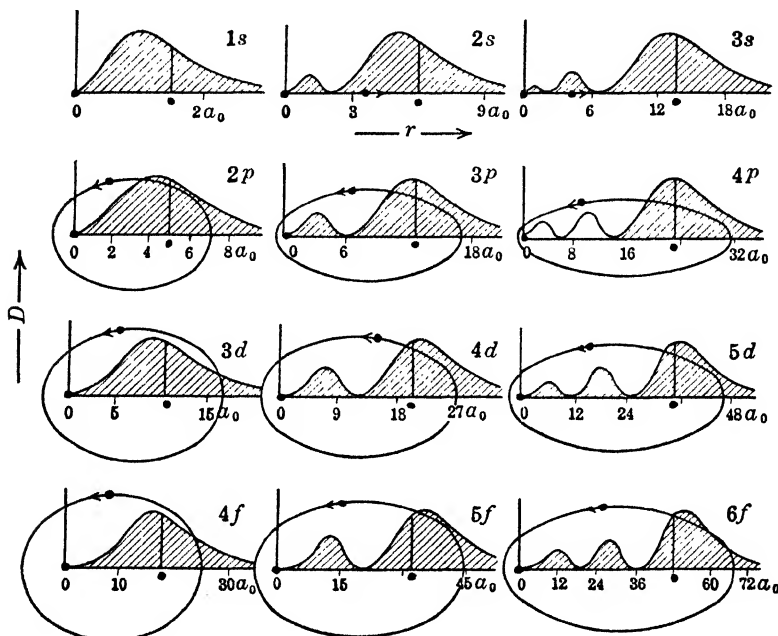

FIG. 10.4. Radial Distribution Function (D) for Different Electronic States of Hydrogen
Atoms and Bohr Orbits for Comparison, Where k is Replaced by $\sqrt{l(l+1)}$

gives plots of D as a function of r/a_0 for the normal ($1s$) and excited states of the hydrogen atom. Because of the occurrence of the factor r^2 in equation (10.12), the value of D vanishes for $r = 0$. With increase in r, the function D passes through a maximum at a value which we shall designate by $r = r_m$, and decreases rapidly with further increase in r, because of the preponderating effect of the exponential factor in the expression for the eigenfunction ϕ_{nlm}.

A simple calculation [2] shows that in the case of the $1s$ state, $r_m = a_0$. That is, the probability of occurrence of the electron in the space surrounding the nucleus has a maximum value at that value of r which according to the Bohr

[1] Ref. H. E. W., p. 68.
[2] Ref. S. D., p. 197 *et seq.*

theory corresponds to the radius of the normal (circular) orbit. Furthermore the values of r_m for the $2p$ and $3d$ states are $4a_0$ and $9a_0$ respectively, which according to the Bohr theory are the values of r for the circular orbits of quantum numbers $n = 2$ and $n = 3$ respectively.

In the Bohr theory the ratio of the minor axis to major axis of an elliptic orbit is given by the value of k/n, where k is the azimuthal quantum number. "In the new theory the latter has to be replaced by $\sqrt{l(l+1)}$. With this modification, the corresponding orbits, as deduced from the older theory, are indicated on each of the plots of D in Fig. 10.4. The origin is taken as one of the foci of each ellipse, so that the distances from the origin along the axis of r to these curves give the maximum and minimum distances of the electron from nucleus according to the Bohr-Sommerfeld theory."

While the new theory replaces the electronic orbit of the Bohr theory by an electron distribution function, it should be observed that the function D always exhibits an exponential decrease with increase in r beyond the maximum value of r as given by the Bohr theory.

(3) **Wave Mechanics Treatment of Electronic Momentum and Angular Momentum of Atom:** According to the Principle of Indeterminism it is impossible to designate the simultaneous position and velocity of an electron with the same degree of exactness, and in this manner we can account for finite values of the distribution function D, discussed in the previous section, for regions of space in which the potential energy, $- Ze^2/r$, is greater (more positive) than would be permitted by classical theory. However, it is possible to calculate a *velocity distribution* function for the electron in any given state, and Fig. 10.5 [1] shows plots of this function for the normal state $(n = 1, l = 0)$ and for the excited state $(n = 2, l = 0)$. The ordinate gives the probability of occurrence of a velocity of the electron given by the value of the abscissa. Thus in the normal state, the most probable velocity is 1.2×10^8 cm. sec.$^{-1}$, while in the excited state this velocity is 0.4×10^8 cm. sec.$^{-1}$. The upper scale

FIG. 10.5. Probability Distribution of Momentum and Velocity in the States $n = 1, l = 0$, and $n = 2, l = 0$ of the Hydrogen Atom

of abscissae gives the momentum expressed in units of $h/(2\pi a_0) = 1.96 \times 10^{-19}$ gm. cm./sec., in accordance with the relation,

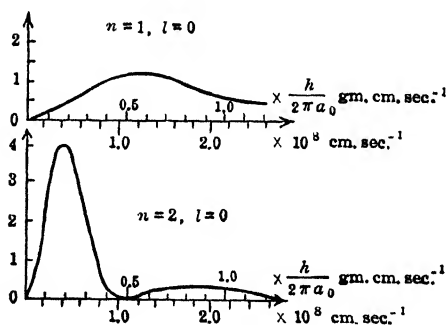$$mv = qh/(2\pi a_0),$$

where q is a pure number.

[1] G. Herzberg, Atomic Spectra and Atomic Structure, p. 48, Prentice-Hall, Inc., New York (1937). (Ref. G. H.)

On the other hand it may be shown that the *angular momentum, p,* of the atom corresponding to any given state of quantum number l has the value

$$p = \frac{h}{2\pi} \sqrt{l(l+1)}. \tag{10.13}$$

Thus for $l = 0$, $p = 0$, which signifies that in this state, the atom as a whole has no angular momentum, in spite of the fact that there is a motion of the electron. In the classical Bohr theory, the value $k = 0$ could not occur, since this would have indicated an oscillatory motion of the electron through the nucleus. As Herzberg writes, "The fact that even in wave mechanics each stationary state of the atom has a perfectly definite angular momentum shows that the atom can still be regarded as consisting of electrons rotating about a nucleus, as in the original Bohr theory. We must not, however, speak of definite orbits."

11. Inner Quantum Number and Electron Spin

(1) **Selection Principle:** According to the Bohr theory, every line in a spectrum originates as a transition between two energy levels. Is the reverse true? That is, given two different levels, is a transition between these levels always possible? The answer is given by observations such as those on the spectral terms in sodium (shown in Fig. 1.5). There it is observed that only those transitions occur for which the change in l is $\Delta l = \pm 1$, while there is no limitation whatsoever as far as changes in the value of n are concerned.* Thus we have the transitions corresponding to $S \rightarrow P$; $P \rightarrow S$; $D \rightarrow P$, $F \rightarrow D$, that is, between levels in adjacent columns, but no transition between levels in the same column or between say S and F levels (except under certain special conditions).

These observations illustrate a rule or *Selection Principle* which may be stated as follows:

The only transitions which are ordinarily observed in spectra are those for which l changes by unity, that is,

$$\Delta l = \pm 1. \tag{11.1}$$

It is the existence of this selection principle that leads to the possibility of sorting out spectral terms into *adjacent* columns such as those shown in Fig. 1.5 for sodium, and Fig. 1.6 for mercury.

While Bohr deduced a selection rule for $k = l + 1$ on the basis of the Correspondence Principle, his arguments may be regarded now as largely of historical interest only.[1]

A much more rigorous basis for the validity of selection principles governing transitions between states of different quantum numbers has been deduced by

---

* For spectral terms arising from single valence electrons, l and L are identical, as explained more fully in a subsequent section.

[1] See discussion pp. 1177–1182, second edition of this Treatise.

the methods of quantum mechanics. In this manner it has been shown that while a selection principle of the form stated above applies to quantum number l, no such restriction applies to the total quantum number n, and this is in agreement with spectroscopic observations.

(2) **Multiplet Levels and Inner Quantum Numbers:** As shown in Fig. 1.5 the spectrum of sodium actually exhibits two sets of P levels, one designated by the subscript $\frac{1}{2}$ and the other by the subscript $\frac{3}{2}$. For any given value of n, these two levels are so close together that lines emanating from them are of nearly the same wave length. The two D-lines of sodium, $\lambda 5890$ and $\lambda 5896$, provide a well-known example of doublet lines such as are observed in the spectra of all the alkali metals. Furthermore, for each set of values of n and l (with the exception of $l = 0$) we observe *two* terms, with a difference in wave numbers, $\Delta \tilde{\nu}$, which varies with n and l in accordance with the following rules:

(1) For any one type of spectral term ($l = $ constant), $\Delta \tilde{\nu}$ *decreases as n increases.*

(2) For a given value of n, $\Delta \tilde{\nu}$ *decreases as l increases.*

Comparing such *doublet* terms having the same values of n and l in the different alkali spectra, it is observed that $\Delta \tilde{\nu}$ increases with the atomic number. Hence, while in the case of Li and Na only doublet P-levels are observed, the D-levels begin to exhibit doublet structures with larger and larger values of $\Delta \tilde{\nu}$ as we proceed from K to Rb and Cs, while $\Delta \tilde{\nu}$ for the two F-levels is so small that the doublet structure is practically unresolvable for even Cs.

As is also evident from Fig. 1.5 the transitions between these doublet levels are governed by a selection principle similar to that observed for the S, P, D and F levels. Thus, instead of the expected four lines as a result of transitions between two doublet D- and P-levels, only *three* are observed.

In the case of calcium, mercury, and other metals of Group II in the Periodic Table, it has been found that the spectral lines belong to two separate systems of S, P, D and F levels. In one system these levels are all *singlets*, while in the other the P, D and F levels are *triplets*. Spectral lines are observed which correspond not only to transitions between levels within one system, but also to transitions between a level in one system and another in the second system ("intercombination" lines). Fig. 1.6 shows the lower levels and a number of the lines in the triplet and singlet systems for mercury, and here also it is observed that a selection principle governs the possible transitions between the one set of levels belonging to a given pair of values of n and l and the other levels belonging to another pair of values of n and l. Denoting the wave number differences between the three component levels for given values of n and l by $\Delta \tilde{\nu}_1$ and $\Delta \tilde{\nu}_2$ it is observed that each of these varies with n and l in a manner similar to that observed in the case of the alkali doublet levels.

Formally the existence of these multiplets may be correlated with the assignment of a third, or so-called *inner quantum number*, j, which differs for each term of a multiplet. In the case of the doublet terms of the alkali metals,

the value of j for the S-term is $\frac{1}{2}$, while the doublet P-terms have the values $\frac{1}{2}$ and $\frac{3}{2}$, and the doublet D-terms, the values $\frac{3}{2}$ and $\frac{5}{2}$. The values of j for the different terms in singlet and triplet systems, as well as in those of higher multiplicity are shown in Table 11.1.

<div align="center">TABLE 11.1</div>

	Singlets	Doublets	Triplets	Quartets
S	0	$\frac{1}{2}$	1	$\frac{3}{2}$
P	1	$\frac{1}{2}, \frac{3}{2}$	0, 1, 2	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$
D	2	$\frac{3}{2}, \frac{5}{2}$	1, 2, 3	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}$
F	3	$\frac{5}{2}, \frac{7}{2}$	2, 3, 4	$\frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}$
G	4	$\frac{7}{2}, \frac{9}{2}$	4, 5, 6	$\frac{5}{2}, \frac{7}{2}, \frac{9}{2}, \frac{11}{2}$

	Quintets	Sextets	Septets	Octets
S	2	$\frac{5}{2}$	3	$\frac{7}{2}$
P	1, 2, 3	$\frac{3}{2}, \frac{5}{2}, \frac{7}{2}$	2, 3, 4	$\frac{5}{2}, \frac{7}{2}, \frac{9}{2}$
D	0, 1, 2, 3, 4	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}$	1, 2, 3, 4, 5	$\frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}, \frac{11}{2}$
F	1, 2, 3, 4, 5	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}, \frac{11}{2}$	0, 1, 2, 3, 4, 5, 6	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}, \frac{11}{2}, \frac{13}{2}$
G	2, 3, 4, 5, 6	$\frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}, \frac{11}{2}, \frac{13}{2}$	1, 2, 3, 4, 5, 6, 7	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \frac{9}{2}, \frac{11}{2}, \frac{13}{2}, \frac{15}{2}$

In designating the different terms of a multiplet, the j-value is indicated as an index at the lower right-hand side, while the degree of multiplicity is indicated by an index at the upper left-hand side. Thus the two terms of the P-doublets for the alkali metals are designated spectroscopically by the symbols $n^2 P_{1/2}$ and $n^2 P_{3/2}$, while the three components of the triplet P terms in the case of elements of Group II are designated $n^3 P_0$, $n^3 P_1$ and $n^3 P_2$.

As in the case of the quantum number l, the quantum number j obeys a selection rule of the form

$$\Delta j = 0, \quad \text{or} \quad \pm 1 \tag{11.2}$$

with the added condition that no transitions can occur from $j = 0$ to $j = 0$.

We thus observe the following transitions in the case of a doublet spectral system (such as that of one of the alkali metals).[1]

$P_{1/2} \rightarrow S_{1/2}$;	$P_{3/2} \rightarrow S_{1/2}$		*two* lines
$D_{5/2} \rightarrow P_{3/2}$;	$D_{3/2} \rightarrow P_{3/2}$;	$D_{3/2} \rightarrow P_{1/2}$	*three* lines
$F_{7/2} \rightarrow D_{5/2}$;	$F_{5/2} \rightarrow D_{5/2}$;	$F_{5\ 2} \rightarrow D_{3/2}$	*three* lines

The D-lines in sodium correspond to the two $P \rightarrow S$ transitions. Since the energy levels corresponding to $D_{5/2}$ and $D_{3/2}$ are much closer than those corresponding to $P_{3/2}$ and $P_{1/2}$, the two lines terminating on the $P_{3/2}$ level are practically merged into one, so that the resulting spectral lines appear as a doublet, except under very high resolving power. Similarly the two transitions from

---

[1] When there is no question regarding the degree of multiplicity, the upper left-hand index is often omitted.

F levels to $D_{5/2}$ appear as a single line, while the transition $F_{5/2} \rightarrow D_{3/2}$ forms the other component of what appears to be a doublet structure. The designation doublet system thus refers to the *spectroscopic terms* or *energy levels*, and not to the resulting spectral lines.

(3) **Electron Spin**: In the case of an atom with a single valence electron, it has been shown that the quantum number *l* corresponds to an angular momentum associated with the motion of the electron, which has the magnitude, in units of $(h/2\pi)$,

$$p = \sqrt{l(l + 1)}. \tag{11.3}$$

An angular momentum can, of course, be represented by a vector and the physical interpretation originally suggested for the quantum number *j* was that it corresponds to the resultant of two angular momentum vectors, one designated by *l*, which is associated with the orbital motion of the electron, and another, designated by *s*, which corresponds to the angular momentum of the rest of the atom or kernel. This led to numerous difficulties in the interpretation not only of the effect of magnetic fields on spectral lines, but also of multiplet terms of higher multiplicity than two.

G. E. Uhlenbeck and S. Goudsmit [1] showed, however, that by introducing the hypothesis of the *spinning electron*, all these difficulties are eliminated and the interpretation of multiplet levels becomes very much simplified. According to this hypothesis, each electron in an atomic system possesses an intrinsic angular momentum whose component in any direction is equal to $s(h/2\pi)$ where $s = \pm \frac{1}{2}$. On the basis of wave mechanisms it is shown that the total angular momentum of spin is $\sqrt{s(s + 1)}$ in units of $(h/2\pi)$. If this angular momentum is combined with that due to the orbital motion of the electron, and represented in units of $(h/2\pi)$ by $\sqrt{l(l + 1)}$, the result is an angular momentum associated with quantum number *j*, and represented, in units of $(h/2\pi)$, by $\sqrt{j(j + 1)}$.

The interaction of these vectors may be illustrated by means of Fig. 11.1. Classically, the vectors *l* and *s* would be combined to form a resultant *j*, as shown in Fig. 11.1(a). That is, $j = l \pm \frac{1}{2}$, where *j* is a multiple of $\frac{1}{2}$. Since, however, the *magnitudes* of these vectors in units of $(h/2\pi)$ are not integral, as indicated above, the model shown in Fig.

Fig. 11.1. Vector Models *a* and *b* for the Composition of Angular Momentum of Electron Spin and of Orbital Motion

11.1(b) has to be used. Thus, while the values of the *quantum numbers* are *l*, *s* and $j = l \pm \frac{1}{2}$, the magnitudes of the corresponding angular momentum vectors (in units of $(h/2\pi)$ for different values of *l* (for a single valence atom) are
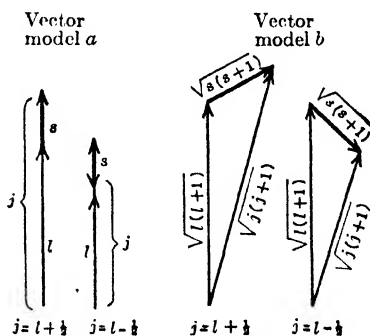
[1] *Naturwiss.*, **13**, 953 (1925); *Nature*, **117**, 264 (1926).

those shown in Table 11.2. It should be noted that for a single electron, the value of this momentum (in units of $h/2\pi$) is

$$p_j = \sqrt{(\tfrac{1}{2})(\tfrac{1}{2} + 1)} = (\tfrac{1}{2})\sqrt{3}. \tag{11.4}$$

TABLE 11.2

l	p_l	$j = l \pm \tfrac{1}{2}$	p_j	θ
0	0	$\tfrac{1}{2}$	$(\tfrac{1}{2})\sqrt{3}$	
1	$\sqrt{2}$	$\tfrac{1}{2}$	$(\tfrac{1}{2})\sqrt{3}$	144° 44′
		$\tfrac{3}{2}$	$(\tfrac{1}{2})\sqrt{15}$	65° 54′
2	$\sqrt{6}$	$\tfrac{3}{2}$	$(\tfrac{1}{2})\sqrt{15}$	135°
		$\tfrac{5}{2}$	$(\tfrac{1}{2})\sqrt{35}$	83° 11′
3	$\sqrt{12}$	$\tfrac{5}{2}$	$(\tfrac{1}{2})\sqrt{35}$	131° 49′
		$\tfrac{7}{2}$	$(\tfrac{1}{2})\sqrt{63}$	60°

Denoting the angle between the vectors l and s by θ, it follows that

$$j(j + 1) = l(l + 1) + s(s + 1) + 2\sqrt{l(l + 1)s(s + 1)}\cos\theta. \tag{11.5}$$
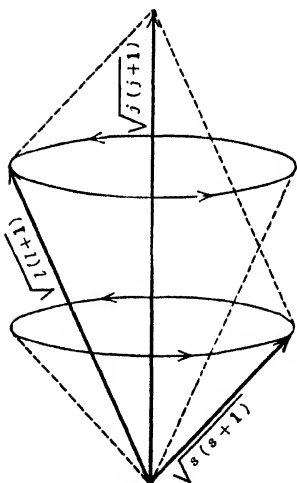
FIG. 11.2. Illustrating the Precession of Angular Momentum Vectors for Spin and Orbital Motion Around Their Mechanical Resultant Represented by J

The value of θ deduced in this manner is given in the last column of Table 11.2. In a subsequent section it will be shown that equation (11.5) is of fundamental significance in calculating the energy due to this coupling of orbit and spin vectors.

This coupling of the l- and s-vectors to form a resultant j corresponds mechanically to a precession of the two components about their resultant, as shown in Fig. 11.2.[1]

For purposes of qualitative discussion the magnitudes of the vectors may be represented (as is done frequently in the following remarks) by s, l and j. But care must be exercised to use the correct magnitudes, as given in Table 11.2, for any quantitative calculations.

Even before the advent of wave mechanics it was recognized that the value $l = 0$ must be assigned to the lowest level of a univalent atom in order to account for the occurrence of a single value of j. And, of course, having assigned the value $l = 0$ to the s-level, the values $l = 1$, 2 and 3 follow from the Selection Principle for the P, D and F levels respectively.

[1] Ref. H. E. W., p. 127.

It is also possible on this basis of assignment of j-values to deduce the relative energy values of the components in any pair of doublet levels. Let us consider the significance of combining the vector $l = 1$ with $s = \frac{1}{2}$. The result of adding these vectors is $j = \frac{3}{2}$, and physically it may be interpreted as indicating that the direction of rotation of the electron is in the same direction as that of the electron in its orbit. On the other hand, if the resultant vector is $j = 1 - \frac{1}{2} = \frac{1}{2}$, the interpretation is that the two directions of rotation are opposed to each other. But, since each angular momentum also carries with it a magnetic field (owing to the rotating charge), it follows that the two magnetic fields will exert an attractive force on each other in the case of opposing rotational directions ($j = \frac{1}{2}$) and that therefore it will require more energy to remove the electron when the atomic system is in the state $j = \frac{1}{2}$, than when the two directions of rotation are similar and the atomic system is in the state $j = \frac{3}{2}$. Consequently, the levels designated as $P_{1/2}$ and $D_{3/2}$ will be lower in the energy diagram than the levels $P_{3/2}$ and $D_{5/2}$ respectively.

(4) **Russell-Saunders Coupling:** In the case of atomic systems containing more than one valence electron, the spectral terms represent energy states which result from (a) attractive forces between the electrons and the nucleus, and (b) repulsive forces between the electrons. Hence the Schroedinger equation for the system will contain potential energy terms due to these two types of interaction. Moreover, account has to be taken of the magnetic interaction of the electronic orbits and spins. Since the exact procedure for dealing with this problem is not known,[1] approximate methods have had to be developed. The one which has proved most useful is that known as the LS- or Russell-Saunders coupling,[2] which is described in the following section.

Let us consider the case of *two* electrons with quantum numbers l_1 and l_2. These correspond to angular momenta of magnitudes $\sqrt{l_1(l_1 + 1)}$ and $\sqrt{l_2(l_2 + 1)}$ respectively. The possible resultant angular momenta are given by the values

$$L = (l_1 + l_2), (l_1 + l_2 - 1), \cdots, (l_1 - l_2), \qquad (11.6)$$

where $l_1 > l_2$. It will be observed that the symbol L represents an angular momentum of magnitude $\sqrt{L(L + 1)}(h/2\pi)$ which results from the interaction of the electronic angular momenta.

In a similar manner the interaction of the spin vectors s_1 and s_2 of the two electrons will be represented by the resultant vector of magnitude $\sqrt{S(S + 1)}h/2\pi$, where the *quantum number S* is given by the relation,

$$S = s_1 + s_2, \qquad \text{or} \qquad s_1 - s_2. \qquad (11.7)$$

Since s_1 and s_2 can each assume only the two discrete values $+\frac{1}{2}$ or $-\frac{1}{2}$, it follows that S can have only the two values 0 or 1. The actual magnitude

[1] E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra, Chapter VI, The Macmillan Company, New York, (1935).

[2] H. N. Russell and F. A. Saunders, *Astrophys. J.*, **61**, 38 (1925). See also ref. H. E. W., Chap. XII.

of the vector, in units of $h/2\pi$ is 0 or $\sqrt{2}$. Again it will be observed that S is used to distinguish the resultant of spin-spin interaction from the individual spin quantum numbers.

The further requirement that

$$J = L + S, \quad L + S - 1, \quad \cdots, \quad |L - S|, \tag{11.8}$$

leads to the appearance, in the case of an atom with two valence electrons, of *two systems* of spectral terms, each associated with one of the two possible values of S. These are indicated in Table 11.3.

<p align="center">TABLE 11.3</p>

Spectral Type	L	J for $S = 0$	J for $S = 1$
S	0	0	1
P	1	1	2, 1, 0
D	2	2	3, 2, 1
F	3	3	4, 3, 2

That is, in one system there is only one value of J for each value of L, in the other there are *three* values of J for each value of L. The former is known as a *singlet* system, the latter, as a *triplet* system. In this manner an interpretation is given for the occurrence of singlet and triplet levels in the spectra of atoms with two valence electrons.

In the case of an atom with three electrons, S can have the two values, $S = \frac{3}{2}$, and $S = \frac{1}{2}$. Associated with the latter will be a system of *doublet* levels, as in the case of atoms with one electron, and corresponding to $S = \frac{3}{2}$, there will be the following values of J for different values of L:

$L = 1$	2	3
$J = \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$	$\frac{7}{2}, \frac{5}{2}, \frac{3}{2}, \frac{1}{2}$	$\frac{9}{2}, \frac{7}{2}, \frac{5}{2}, \frac{3}{2}$

Thus *four* multiplet levels are associated with the value $S = \frac{3}{2}$. The system is said to be of the *quartet* type.

As we proceed in the periodic table from Group I to Group VIII it is observed that the spectral terms exhibit periodic variations in regard to the maximum degree of multiplicity, and that the maximum value of the multiplicity increases with the value of J for the S-term. This is illustrated in Table 11.4 for the elements from K (At. No., 19) to Ni (At. No., 28). The most striking feature brought out by this table is that the *multiplicity alternates between even and odd* as we pass from K to Ni. Furthermore for atoms with an odd number of valence electrons the multiplicity is even, and it is odd for an even number of valence electrons.

TABLE 11.4

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
	Singlets		Singlets						Singlets
Doublets		Doublets		Doublets				Doublets	
	Triplets		Triplets		Triplets		Triplets		Triplets
		Quartets		Quartets		Quartets		Quartets	
			Quintets		Quintets		Quintets		Quintets
				Sextets		Sextets		Sextets	
					Septets		Septets		
						Octets			

It is the presence of these multiplet levels and the resultant possibilities of transitions in each system *as well as between systems* that give rise to the extremely complex nature of a large number of spectra, such as those of Ti, Cr, Mn, Fe and other elements. In fact, it was only after the Bohr theory of energy levels had been postulated and the more simple types of spectra had been interpreted from this point of view that any progress could be attained in unravelling these more complicated spectra, so that it is only within the past few years that it has been found possible to formulate energy level diagrams for these cases. As an illustration of such an investigation the work of H. N. Russell on the spectrum of titanium may be mentioned. This spectrum has been found by him to consist of seventeen series divided between singlet, triplet and quintet systems.

On the basis of equations (11.6), (11.7) and (11.8) it is possible, as illustrated above, to account for the different types of multiplicity and for the assignment of J values which are shown in Table 11.1. From equation (11.8) it follows that for $L > S$, the number of possible values for J for a given value of L is $2S + 1$. (This is most readily deduced by putting $L - S = n$, so that the values of J are $n + 2S$, $n + 2S - 1$, $\cdots$ $n + 2S - 2S$.) Also, for $L < S$, the number of possible values for J for a given value of S is $2L + 1$. This leads to the conclusion that for $L = 0$ (S-terms), there is only *one* value of J, viz. $J = S$. That is the S-level is always single, as shown in Table 11.1. Denoting the *degree of multiplicity* by r ($r = 1$ for singlets, $r = 2$ for doublets, etc.), it follows that

$$r = 2S + 1, \tag{11.9}$$

which is again illustrated by Table 11.1.

It should be added in this connection that the Selection Principle applies to L in the same manner as to the electronic quantum number l, that is

$$\Delta L = \pm 1, \tag{11.10}$$

although $\Delta L = 0$ is also permissible. In addition there is the rule that for the electron making the transition, $\Delta l = \pm 1$. Thus, the state $L = 1$, $l_1 = 1$,

$l_2 = 0$ cannot combine with a state $L = 2$, $l_1 = 3$, $l_2 = 3$, although a transition between these two states would not violate the rule $\Delta L = \pm 1$.

Furthermore, for Russell-Saunders coupling $\Delta S = 0$, that is no transitions are permitted from terms of one type of multiplicity to terms of another type of multiplicity. However, such *intercombination* lines are actually observed, especially for elements of higher atomic number, which means that spin-orbit interaction becomes more prevalent in these cases.

12. Effect of Magnetic and Electrostatic Fields on Spectral Terms

(1) **Zeeman Effect:** [1] The following description of this effect is taken from F. K. Richtmyer's "Introduction to Modern Physics." [2]

"In 1896 Zeeman discovered that spectral lines are split up into components when the source emitting the lines is placed in a very strong magnetic field, and, further, that these components are polarized. The simplest case is shown in Fig. 12.1 where a represents a line before the magnetic field is turned on. If the field be turned on and the line be viewed at *right angles* (R) to the direction of the field, the line is seen to be triple with components σ_1, π and σ_2. The central line π has the same wave-length as the original line a but is plane polarized in a plane at *right angles* to the magnetic field H, the direction of polarization being indicated by the double arrow above the line. The other two components, σ_1 (left, shorter wave length) and σ_2 (right, longer wave length) are plane polarized in a direction *parallel* to the magnetic field.

FIG. 12.1.   Effect of Magnetic Field on Spectral Lines (Zeeman Effect)

"If the pole pieces of the electromagnet be drilled through longitudinally so that one may view the flame in a direction parallel to the magnetic field, only two components are seen, as shown at P. These two lines have the same respective wave-lengths as the outside components in the previous case, but they are *circularly* polarized in opposite directions, as shown by the arrows above the lines. (The magnetic field, in this latter case, is directed toward the reader.)"

Since the direction of vibration of the electric vector is at right angles to the plane of polarization, the π-component corresponds to vibration in a direction parallel to that of the field (hence the symbol π, for "parallel"), and the σ-components correspond to vibrations of the electric vector in a direction at right angles to that of the field (the symbol σ for "senkrecht," that is "at right angles").

It was observed that the *change in frequency*, $\Delta\nu_n$, of each outside component is given by the relation

$$\Delta\nu_n = \frac{e}{2m_0} \cdot \frac{H}{2\pi}, \qquad (12.1)$$

where H = intensity of field.

---

[1] This topic is dealt with very comprehensively in the treatise, Zeemaneffekt und Multiplett Struktur der Spektral Linien by E. Back and A. Landé, Julius Springer, Berlin, 1925.

[2] First edition, page 143.

Substituting the value $e/m_0 = 1.7591 \times 10^7$ e.m.u. gm.$^{-1}$ and expressing H in gauss,

$$\sigma = \Delta\nu_n = 1.400 \times 10^6 \text{ H sec.}^{-1}. \qquad (12.2a)$$

The change in *wave number* is given by

$$\Delta\tilde{\nu}_n = \frac{\sigma}{c} = 4.670 \times 10^{-5} \text{ H cm.}^{-1}. \qquad (12.2b)$$

The resolution into three components with separation given by the above equation could be accounted for by Zeeman on the basis of the classical electromagnetic theory by applying Lorentz's electron theory of matter.[1] Indeed the Zeeman effect was used to obtain very accurate determinations of e/m_0.

However, it was found that only relatively few of the spectral lines show this type of resolution in magnetic fields, and that most spectral lines exhibit a much more complex resolution. Instead of three components in a transverse magnetic field, there are observed a larger number, some having the same state of polarization as the π-component (class π) in Fig. 12.1 and others similar to the σ-components, the number of each class varying with the spectral type of the line.

Consequently the designation of *normal* effect was applied to those cases in which the observed displacement is given by equation (12.1) or (12.2) while the designation of *anomalous* Zeeman effect came into use for more complex types of resolution.

Further investigation of the behavior of different spectral

Fig. 12.2. Zeeman Patterns for Different Spectral Lines

lines in magnetic fields led to the deduction by spectroscopists of several important empirical generalizations, as follows:

(1) The spectral lines belonging to any given type of series (such as the principal or diffuse series in the alkali and alkaline earth groups) exhibit the
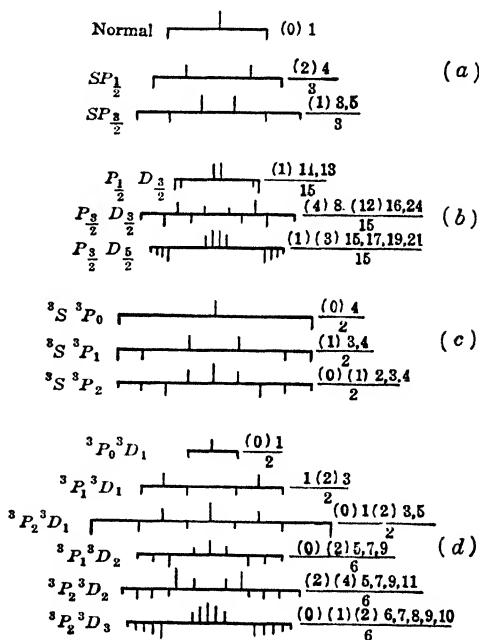
[1] For this explanation the reader is referred to Richtmeyer's book.

same type of resolution in a magnetic field. (Obviously this rule could then be used as a guide for determining the spectral type of an unclassified line from its behavior in magnetic fields.)

(2) The lines corresponding to the difference between terms of a series A and another series B exhibit the same pattern as those corresponding to the difference between terms of series B and those of series A.

(3) The components produced by resolution in a magnetic field are located symmetrically (with respect to changes in frequency or wave number) about the original line.

(4) The value of $\Delta\nu$, the change in frequency (or $\Delta\tilde{\nu}$, the change in wave number) for any one component is always a rational multiple (not necessarily integral) of the value $\Delta\nu_n$ (or $\Delta\tilde{\nu}_n$) calculated from (12.1) or (12.2).

As an example, we may consider the resolution in a magnetic field of lines of the principal series in the alkali metals, for instance the D-lines of sodium ($\lambda 5890$ and $\lambda 5896$). This is diagrammatically represented in Fig. 12.2 (a) in which the π- and σ-components are distinguished by short vertical lines above and below the horizontal line respectively. The relative intensities of the components are indicated quantitatively by the length of the vertical lines in the diagram, while the relative separation of the components (that is, the value of $\Delta\nu$) is also indicated quantitatively by comparison with the pattern for the normal Zeeman effect shown at the top in Fig. 12.2.

Lines of the diffuse series of the alkali metals (e.g., $\lambda 8183$ and $\lambda 8195$, Fig. 1.5) exhibit a Zeeman pattern of the type shown in Fig. 12.2 (b), while for the transitions $S–P$ and $P–D$ in the triplet series the Zeeman patterns are of the types shown in (c) and (d) respectively. Illustrations of these transitions are found in the energy level diagrams for calcium and mercury (Fig. 1.6.)

To understand the significance of the numerical values given in the right-hand side of Fig. 12.2, it is necessary to discuss briefly the classical quantum theory of the Zeeman effect.[1]

In accordance with Bohr's theory, we must look for the observed resolution of any given line as due to the effect of a magnetic field on the initial and final states of the atomic system which are involved in the production of the line. The interpretation given by Bohr rests upon a theorem deduced by Larmor together with an application of the method of the perturbations used in astronomical calculations.

For an electronic orbit of angular momentum,

$$p = l(h/2\pi),$$

---

[1] In addition to the references already given, the discussion of the anomalous Zeeman effect given by A. Landé in *Ergeb. exakt. Naturwiss.*, **2**, 147 (1923) should be consulted. Fig. 12.2 is taken from this source. It should be noted, however, that the spectral notation and assignment of j-values have been changed since that date. For more recent discussion of this topic the reader should consult the following: E. C. Stoner, Magnetism and Matter, Chapter VI, Methuen and Co., London (1934), (Ref. E. C. S.), also refs. H. E. W., and G. H.

the magnetic moment is given (on classical basis) by the relation [1]

$$\mu = -\frac{e}{2mc}p = -\frac{e}{2mc}\cdot\frac{lh}{2\pi} = l\mu_B, \qquad (12.3)$$

where *e is measured in e.s.u.*, and the negative sign indicates that the magnetic moment has the opposite direction to that of the angular momentum.

For $l = 1$, $\mu = 9.2720 \times 10^{-21}$ erg gauss^{-1}. This constitutes the unit of magnetic moment and is known as the *Bohr magneton.* It is usually designated by the symbol μ_B, and corresponds to $6.023 \times 10^{23}\mu_B = 5582$ erg gauss^{-1} per gram atom.

According to Larmor's theorem the effect on this magnetic moment of a field of intensity H is that of imposing upon the electronic motion *a precession of the orbit about the direction of* H, of frequency,

$$\omega_H = \frac{\mu H \cos\theta}{h} = \frac{e}{2mc}\cdot\frac{H}{2\pi}\,l\cos\theta = m\sigma, \qquad (12.4)$$

where θ is the angle between the plane of the orbit and the direction of H, and

$$\sigma = \frac{eH}{4\pi mc}. \qquad (12.5)$$

Thus $\sigma = \Delta\nu_n$, the change in frequency which was introduced in equation (12.2a). This "Larmor" precession is illustrated in Fig. 12.3 [2]

The theory of perturbations leads to the conclusion that for ω_H small in comparison with ω the frequency of rotation of the electron in its orbit, the *change in energy* due to the presence of the field is given by

$$\Delta E = h\omega_H = hm\cdot\sigma, \qquad (12.6)$$

where obviously ΔE may be positive or negative in consequence of the presence of the factor $\cos\theta$ in (12.4).

We now introduce the assumption that the orbit can orient itself in a magnetic field only in certain definite directions such that $l\cos\theta = m$ is *an integral value.* That is, the only possible values of $l\cos\theta$ are the integral values
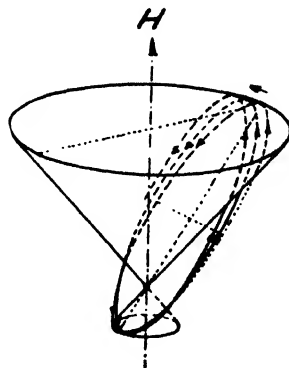
FIG. 12.3. Larmor Precession of Electronic Orbit in Magnetic Field

$$m = l, \qquad l - 1, \qquad \cdots - (l - 1), \qquad -l.$$

---

[1] This expression for μ is the one most frequently used.

[2] Taken from E. Buchwald, Das Korrespondenzprinzip, F. Vieweg & Sohn, Braunschweig, 1923, p. 63.

We have thus introduced a fourth or *magnetic quantum number, m,* whose magnitude gives the number of units of magnetic moment of the orbit resolved in a direction parallel to that of the field.

That is, the energy of the orbit in a field is given by

$$E + \Delta E = E + h\sigma \cdot m,$$

where E is the energy of the unperturbed orbit.

According to the principle of correspondence, this frequency must appear in the radiation emitted, in the form

$$\nu = \Delta n \cdot \omega + \Delta m \cdot \sigma,$$

where Δn represents the change in total quantum number, and Δm the change in magnetic quantum number.

But since m is a measure of angular momentum about an axis of symmetry the same principle of selection must apply as for the inner quantum number j, that is, only those transitions can occur for which

$$\Delta m = \pm 1, \quad \text{or} \quad 0.$$

Hence we must have

$$\nu = \nu_0 \pm \sigma \quad \text{or} \quad \nu_0,$$

where ν_0 is the frequency in absence of magnetic field, and ν is the frequency in presence of a field.

This theory thus leads to the conclusion that every spectral line should be resolved, in a magnetic field, into triplets (*normal* Zeeman effect). In order to account for the so-called "anomalous" effect, it is necessary to introduce into the simple classical theory the concept of electron spin together with the additional hypothesis, suggested by Uhlenbeck and Goudsmit, that *for the electron the ratio between the total magnetic moment and angular momentum is twice that required by Larmor's theorem*, that is,

$$\mu_e = -\frac{2e}{2mc}\, p$$

$$= -\frac{he}{4\pi mc}\, 2s\sqrt{s+1} \tag{12.7}$$

$$= 1.73\mu_B. \tag{12.8}$$

As has been pointed out, the angular momentum corresponding to any energy state in the case of an atomic system is determined by the magnitude of the quantum number J, which is obtained as a result of the LS coupling. If it were not for the anomalous relation between angular momentum and magnetic moment which is expressed by equation (12.7), the change in energy in a magnetic field for a level of quantum number J, would be given by the

relation (analogous to equation (12.6))

$$\Delta E = Mh\sigma, \tag{12.9}$$

where $M = J, J - 1, \cdots, - J$.

That is, the energy level would be split up into $2J + 1$ levels in presence of a field, and these levels would be spaced at equal intervals of magnitude $h\sigma$. But in consequence of equation (12.7), the value of ΔE actually observed is given by a relation of the form,

$$\Delta E = Mgh\sigma, \tag{12.10}$$

where g is the so-called "splitting" factor for which Landé deduced the empirical relation

$$g = 1 + \frac{J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)}. \tag{12.11}$$

This relation has been confirmed subsequently by considerations based on the Uhlenbeck-Goudsmit concept and the use of quantum mechanics.

The derivation of equation (12.11) is of interest, since a similar argument applies to the derivation of the difference in energy for two terms of a multiplet level.[1]

In accordance with equations (12.3) and (12.7) the magnetic moments of the orbital and spin motions of an electron are respectively,

$$\mu_l = \mu_B\sqrt{l(l + 1)} \quad \text{and} \quad \mu_r = 2\mu_B\sqrt{s(s + 1)}. \tag{12.12}$$

We shall consider the case of two electrons for which LS coupling is valid. The two spins (s_1 and s_2) form a resultant of quantum number S. The vector sum of the two magnetic moments projected on that of S is

$$\begin{aligned}\mu_S &= \{\sqrt{s_1(s_1 + 1)}\cos(s_1S) + \sqrt{s_2(s_2 + 1)}\cos(s_2S)\}2\mu_B \\ &= 2\sqrt{S(S + 1)}\mu_B.\end{aligned} \tag{12.13}$$

Similarly the total magnetic moment due to l_1 and l_2, projected on the vector of magnitude $\sqrt{L(L + 1)}$ is

$$\mu_L = \sqrt{L(L + 1)}\mu_B. \tag{12.14}$$

Projecting μ_S and μ_L on the resultant J of the vectors S and L, we derive the equation

$$\mu_J = \{\sqrt{L(L + 1)}\cos(LJ) + 2\sqrt{S(S + 1)}\cos(SJ)\}\mu_B. \tag{12.15}$$

But

$$J(J + 1) = L(L + 1) + S(S + 1) + 2\sqrt{L(L + 1)S(S + 1)}\cos(LJ),$$

[1] This derivation is based on the discussion by H. E. White, *op. cit.*, Chap. XIII, also G. Herzberg, *op. cit.* pp. 106–111.

and

$$L(L + 1) = J(J + 1) + S(S + 1) + 2\sqrt{J(J + 1)S(S + 1)}\cos(SJ),$$

in consequence of the rules for the composition of momentum vectors. Substituting for $\cos(LJ)$ and $\cos(SJ)$ from these equations in equation (13.15), it follows that

$$\mu_J = g\sqrt{J(J + 1)}\mu_B, \qquad (12.16)$$

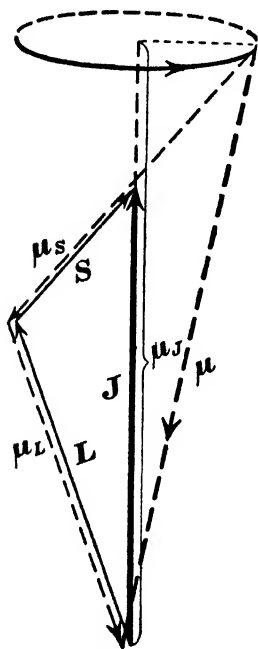where g is given by equation (12.11).

Figure 12.4 and the remarks on its significance, taken from the discussion of this topic by G. Herzberg, illustrate the relation between the total angular momentum vector J and the vector gJ which corresponds to the resultant magnetic moment. The lengths of the vectors are proportional to the angular momentum vectors $\sqrt{L(L + 1)}$, and so forth. If it were not for the factor 2 postulated in the ratio between μ_S and p for the electron, the vector representing the resultant of μ_L and μ_S would be equal to $\sqrt{J(J + 1)}\mu_B$. But actually μ_S is double the length corresponding to S. "The resultant μ therefore falls," as Herzberg points out, "not in the direction of J, but in the direction shown, which is different from J and precesses with L and S about the direction of the total angular momentum. Since this precession is, in general, much faster than the Larmor precession, usually only the component of μ in the J direction, μ_J, need be considered in calculating the magnetic effect." The magnitude of μ_J is, as shown already, given by equation (12.16).

The fact that g is determined by the values of J, L and S, evidently accounts for the empirical generalizations mentioned already, which were deduced from observations on the anomalous Zeeman effect.

FIG. 12.4. Illustrating Landé's g-Formula for Addition of Magnetic Moments

From equations (12.10) and (12.11) it follows that an energy level of quantum number J exhibits in a magnetic field $2J + 1$ levels with displacements in wave number given by the relation

$$\Delta\tilde{\nu} = Mg\,\Delta\tilde{\nu}_n, \qquad (12.7)$$

where $\Delta\tilde{\nu}_n$ is defined by equation (12.2).

For transitions between stationary states the Principle of Selection leads to the conclusion

$$\Delta M = 0 \text{ or } \pm 1.$$

For individual electrons we shall use the small letter m, to indicate the magnetic quantum number, since it is identical with the number designated by the same symbol which was deduced in the solution of the Schroedinger equation in a previous section. Table 12.1 gives values of m, g and mg for different doublet terms, such as are observed in the spectra of atoms containing a single valence electron (e.g., the alkali metal group).

TABLE 12.1

Term	l	j	g	m	mg
$^2S_1$	0	$\frac{1}{2}$	2	$\pm \frac{1}{2}$	± 1
$^2P_1$	1	$\frac{1}{2}$	$\frac{2}{3}$	$\pm \frac{1}{2}$	$\pm \frac{1}{3}$
$^2P_2$	1	$\frac{3}{2}$	$\frac{4}{3}$	$\pm \frac{3}{2};\ \pm \frac{1}{2}$	$\pm \frac{6}{3};\ \pm \frac{2}{3}$
$^2D_2$	2	$\frac{3}{2}$	$\frac{4}{5}$	$\pm \frac{3}{2};\ \pm \frac{1}{2}$	$\pm \frac{6}{5};\ \pm \frac{2}{5}$
$^2D_3$	2	$\frac{3}{2}$	$\frac{6}{5}$	$\pm \frac{5}{2};\ \pm \frac{3}{2};\ \pm \frac{1}{2}$	$\pm \frac{15}{5};\ \pm \frac{9}{5};\ \pm \frac{3}{5}$

Thus in a magnetic field, there are *two* ^2S levels; *six* ^2P levels and *ten* ^2D levels, or more generally, *the total number of possible states of an atomic system with single valence electron, for given value of l, in a weak magnetic field, is equal to $2(2l + 1)$.*

A graphical illustration of this splitting in the case of a $^2P_{3/2}$ term is shown in Fig. 12.5.[1] The vector j is shown in the four allowed positions with the
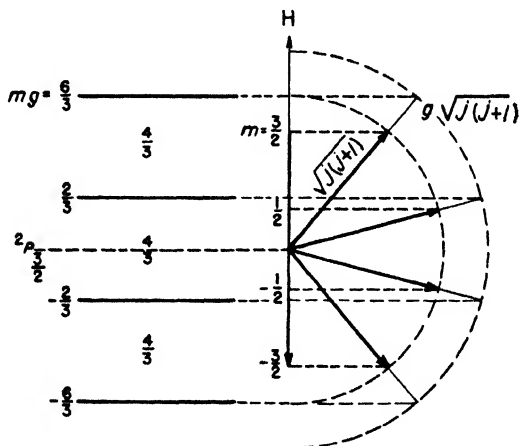

FIG. 12.5. Schematic Orientation Diagram of an Atom in a ^2P State Showing the Resultant Zeeman Levels in a Weak Magnetic Field

associated values of m. The presence of the factor g leads to the relative spacing of the levels which is shown at the left.

[1] Ref. H. E. W., p. 159. In the case of terms arising from single electrons, the symbol j is frequently used instead of J.

By means of the values of mg given in Table 12.1, the effect of weak magnetic fields on different lines may be calculated.   As an illustration we shall consider the doublet D lines in Na which correspond to the transitions ${}^2S_{1/2} - {}^2P_{1/2}$ and ${}^2S_{1/2} - {}^2P_{3/2}$.
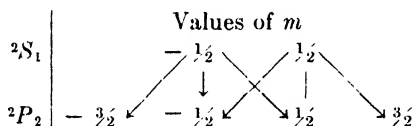
For

$$ {}^2S_{1/2} \quad \frac{\Delta\nu}{\Delta\nu_n} = mg = \pm\,1, $$

and for

$$ {}^2P_{1/2} \quad \frac{\Delta\nu}{\Delta\nu_n} = mg = \pm\,\tfrac{1}{3}. $$

Hence for ${}^2S_{1/2} - {}^2P_{1/2}$, $\dfrac{\Delta\nu}{\Delta\nu_n} = \tfrac{4}{3}; \tfrac{2}{3}; - \tfrac{2}{3}; - \tfrac{4}{3}$.   (See Fig. 12.2a.)

In the case of ${}^2S_{1/2} - {}^2P_{3/2}$ the only transitions in accord with the selection principle are those indicated in the following diagram.

Consequently the possible values of $\Delta\nu/\Delta\nu_n = mg$ are given by $\pm\,\tfrac{5}{3}, \pm\,\tfrac{3}{3}$ and $\pm\,\tfrac{1}{3}$.   (See also Fig. 12.2a.)

It should be observed that it can be shown theoretically that $\Delta m = 0$ yields π-components, and $\Delta m = \pm\,1$, σ-components in the Zeeman pattern. Thus the components for which $mg = \pm\,\tfrac{2}{3}$ in the first case, and the components for which $mg = \pm\,\tfrac{1}{3}$ in the second case are π-components.

These values of mg are indicated conventionally by the notation shown in Fig. 12.2 on the right-hand side.   Thus the notation (2),4/3 for the line $SP_{1/2}$ is used to designate the values $mg = \pm\,\tfrac{2}{3}, \pm\,\tfrac{4}{3}$.   Furthermore the π components are indicated by the brackets around the corresponding value of mg.

While Table 12.1 gives values of m and mg for doublet terms, tables of values for other types of spectral terms are given in the more detailed publications to which reference has been made already.

(2) **Paschen-Back Effect:** With increase in field strength, the magnetic splitting increases and finally exceeds the multiplet splitting.   Under these conditions, as observed by Paschen and Back, the anomalous Zeeman effect changes over to the normal due to the fact that the LS- coupling is broken, and each of the vectors S and L precesses about the direction of the magnetic field. As a result, each of the vectors is quantized separately, the L-vector giving rise to levels of quantum number $M_L = L, L - 1, \cdots, - L$, and the S-vector to levels of quantum number $M_S = S, S - 1, \cdots, - S$.

To a first approximation the change in energy is given by

$$ \Delta E = h\sigma M_L + 2h\sigma M_S \tag{12.19} $$

(since the magnetic moment associated with the S-vector is double the angular momentum, as for a single electron).

The selection rules governing transitions between levels are as follows:

$$\left.\begin{array}{l} \Delta M_L = 0, \quad \text{or} \quad \pm 1 \\ \\ \Delta M_S = 0. \end{array}\right\} \tag{12.20}$$

and

From equation (12.19) it follows that for very strong fields,

$$g = \frac{M_L + 2M_S}{M_L + M_S}. \tag{12.21}$$

As we pass from weak to strong fields, the separation between the components of a given spectral term, produced by the field, changes, but according to a rule proposed in 1923 by W. Pauli, *the sum of the g-values for a given value of M remains constant* for all field strengths. This is known as Pauli's *g permanence* rule and is illustrated in Table 12.2.[1]

TABLE 12.2

Term	$M = 2$	$M = 1$	$M = 0$	$M = -1$	$M = -2$	
$^3P_2$	$3/2$	$3/2$	$3/2$	$3/2$	$3/2$	
$^3P_1$		$3/2$	$3/2$	$3/2$		Weak fields
$^3P_0$			$0/0$			
$^3P_2$	$3/2$	2		1	$3/2$	
$^3P_1$		1		2		Strong fields
$^3P_0$						
Σg	$3/2$	3	$9/6$	3	$3/2$	

"For $^3P_0$, $M = 0$, g is indeterminate in all fields."

An extension of this is *Pauli's g-sum* rule which states that *the sum of the g factors for a given M, of a given electron configuration, is constant.* Thus Σg for the $^3P_0$, $^3P_1$, $^3P_2$ and $^1P_1$ terms (which are due, as shown in Section 15.4, to the sp configuration) is a constant for any given value of M.

(3) **Space Quantization:** [2] In a previous section (12.1) it was pointed out that for an atomic system possessing a resultant angular momentum of magnitude $p = (h/2\pi)\sqrt{J(J + 1)}$, there exist $2J + 1$ possible orientations in a magnetic field, corresponding to the different integral values of the magnetic quantum number,

$$M = J, J - 1, \cdots, -J.$$

[1] Ref. H. E. W., p. 240.

[2] For more detailed discussion see ref., E. C. S., Chap. VII, and R. G. J. Fraser, Molecular Rays. The Macmillan Company, New York (1931).

Thus the state designated by J is degenerate in absence of a field, since there are $2J + 1$ eigenfunctions associated with the same eigenvalue. But in presence of a magnetic field this degeneracy is removed and there result $2J + 1$ levels which are located symmetrically about the value for the unperturbed state, the magnitude of the separation increasing, as in the Zeeman effect, with increase in field strength.

Associated with each value of M there will be a magnetic moment, the component of which, in the direction of the field, is given by the relation

$$\mu = Mg\mu_B, \qquad (12.22)$$

where g is Landé's splitting factor.

The existence of this space quantization was first demonstrated by O. Stern and W. Gerlach [1] by means of an arrangement which is shown diagrammatically in Fig. 12.6.[2] A stream of atoms emitted through the opening O' in
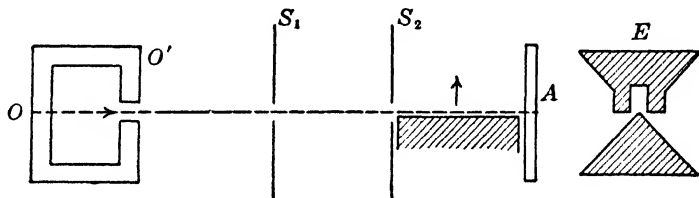
Fig. 12.6.   Arrangement for Stern-Gerlach Experiment

an oven O is defined by the slits S_1 and S_2 and condensed on a plate A, after passing through the inhomogeneous field produced by an electromagnet with pole pieces having the cross-sectional form shown at the right. "In such a field, a body with a magnetic moment is subject, not only to a force moment tending to turn the direction of the magnetic moment into a field direction, but also to a deflecting force due to the difference in field strength at the two poles of the body. Depending on its orientation, the body will therefore be driven in the direction of increasing or decreasing field strength. Suppose we now send through such an inhomogeneous field atoms possessing a magnetic moment. If atoms with all possible orientations to the field are present, a sharp beam should be drawn into a band. Actually, a splitting of the beam into $2J + 1$ different beams takes place. This experiment shows unambiguously that in a magnetic field not all orientations to the field, but only $2J + 1$ discrete directions, are possible." [3]

Table 12.3 gives the values of g and Mg, and the nature of the Stern-Gerlach pattern for each of a series of spectral terms.

[1] *Ann. Physik,* **74,** 673 (1924) and in subsequent papers in *Z. Physik.*
[2] Ref. E. C. S., p. 215.
[3] Ref. G. H., p. 100.

TABLE 12.3

Normal State	g	Mg					Stern-Gerlach pattern
$^1S_0$	$0\frac{.}{0}$			0			
$^1P_1$	1		-1	0	$+1$		
$^1D_2$	1	-2	-1	0	$+1$	$+2$	
$^2S_{1/2}$	2		-1		$+1$		
$^2P_{1/2}$	$\frac{2}{3}$		$-\frac{1}{3}$		$+\frac{1}{3}$		
$^2P_{3/2}$	$\frac{4}{3}$	$-\frac{6}{3}$	$-\frac{2}{3}$		$+\frac{2}{3}$	$+\frac{6}{3}$	
$^3S_1$	2		-2	0	$+2$		
$^3P_0$	$0\frac{.}{0}$			0			
$^3P_1$	$\frac{3}{2}$		$-\frac{3}{2}$	0	$+\frac{3}{2}$		
$^4S_{3/2}$	2	-3	-1		$+1$	$+3$	
$^5S_2$	2	-4	-2	0	$+2$	$+4$	

It will be observed that for $J = 0$, $\mu = 0$ and consequently atoms for which the spectral term corresponding to the normal state has this value of J, are diamagnetic. This is observed in the case of Zn, Cd, Hg and the rare gases, which is in accordance with the fact that the spectral terms of the normal states are of type $^1S_0$. In the case of atoms of the alkali metals, it was observed that the beam of atoms after passing through the field forms two spots located symmetrically about the point of incidence of the atoms in absence of a field, at distances corresponding to the value $\mu = \mu_B$, that is, to $Mg = 1$. Hence $J = \frac{1}{2}$, which is in agreement with the value assigned to the normal states of these atoms ($^2S_{1/2}$).

(4) **Stark Effect:** [1] In presence of a strong electric field, the spectral lines are resolved into components in a manner which is analogous to that observed in magnetic fields. The following description of the conditions under which this phenomenon is observed is quoted from F. K. Richtmeyer.[2]

"An effect of an electric field, somewhat analogous to the Zeeman effect, was discovered by Stark, in 1913, and is known as the 'Stark effect.' It is observed in the well-known 'canal rays' when these are moving in an electric field of several thousand volts per centimeter. The

[1] For more detailed discussion see ref. H. E. W., Chap. XX, which gives an extensive list of references.

[2] Ref. F. K. R., First Edition, p. 325.

arrangement for producing the Stark effect is shown diagrammatically in Fig. 12.7.   *A* and *C* are, respectively, the anode and cathode in a glass tube, the gas in which may be maintained at such a pressure that the Crookes' dark space in front of *C* is several centimeters long.   *C*
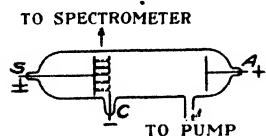

TO SPECTROMETER

TO PUMP

Fig. 12.7.   Arrangement for Observing Stark Effect

is perforated with small holes through which pass in cylindrical bundles luminous streams of atoms of the gas which have acquired a positive charge immediately in front of *C*. These streams of atoms are the canal rays.   A third terminal *S* is placed immediately behind *C*, at a distance of a few millimeters, and an electric field of several thousand (20,000 and up) volts per centimeter is maintained between *S* and *C*. For the 'transverse' Stark effect, light from the canal rays enters the spectroscope in the direction of the arrow.   Stark observed that the lines in the spectrum emitted by the canal rays when no field exists between *S* and *C*, are split up, when the field is applied, into numerous components somewhat after the manner of the Zeeman effect, the lines being polarized, some of them parallel to the field (π components), others perpendicular (σ components)."

Illustrations of the resolution of the Balmer lines of hydrogen and some of the helium lines have been published by J. S. Foster.[1]   While classical electromagnetic theory fails to account for this phenomenon, an explanation based on the Bohr-Sommerfeld theory was given by P. Epstein[2] and K. Schwarzschild.[3] Bohr[4] has shown that the problem of the Stark effect may be dealt with rather simply by application of the Correspondence Principle, and the following discussion of his interpretation is taken from Van Vleck's "Quantum Principles."[5]

While in weak electrostatic fields, the separation of the components for a hydrogenic atom is relatively small and varies as F^2, where F denotes the field strength, the separation becomes proportional to the first power of F in strong fields.   Under these conditions, it is found that the energy levels are given by

$$E = -\frac{Z^2 Rch}{n^2} + \frac{3h^2 n n_F}{8\pi^2 Zem} F. \qquad (12.23)$$

"Here n is the principal quantum number, and n_F is a second quantum number introduced by the addition of the field.   It may be proved that n_F/n is approximately equal to $\epsilon \cos \theta$, where ϵ is the eccentricity and θ is the angle between the semi-major axis and the direction of the field.   Both ϵ and θ execute large slow or 'secular' oscillations, but their product remains very approximately constant.   The new frequency introduced by the field is given by

$$\sigma = \frac{1}{h} \cdot \frac{\partial E}{\partial n_F} = \frac{3hnF}{8\pi^2 Zem}, \qquad (12.24)$$

and it can be proved that this is the frequency with which the 'electrical

[1] *Phys. Rev.*, **23**, 667 (1924); *J. Franklin Inst.*, **209**, 585 (1930).

[2] *Ann. Physik*, **50**, 489 (1916).

[3] *Sitzungsber. Berl. Akad. Wiss.*, 1916, p. 548.

[4] *Proc. Phys. Soc.* (London), **35**, 275 (1923).

[5] Pages 62–66.

center' describes an elliptical harmonic motion in a plane perpendicular to the axis of the field."

The "electrical center" is a point situated midway between the focus (at which the nucleus is located) and the center of the elliptic orbit. The precession of the orbit is illustrated in Fig. 12.8.[1] In this figure the original position of the orbit is indicated as oriented at a certain angle with respect to the XY plane which is perpendicular to the direction of the electric field. Application of this field causes the orbit to precess around the nucleus K in such a manner that the electrical center, M, describes an orbit in a plane parallel to that of XY, as shown in the diagram.
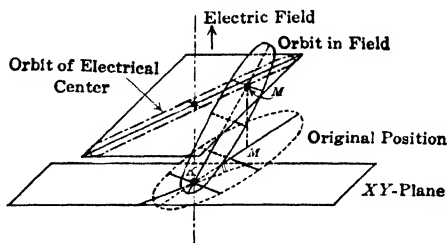
Fig. 12.8. Precession of Electronic Orbit in Strong Electric Field (Stark Effect)

Application of the Correspondence Principle to this motion shows that the frequency of the radiation emitted is given, for small values of both ω (the frequency of revolution in the orbit) and σ, by the approximate relation

$$\nu = (n'' - n')\omega + (n_F'' - n_F')\sigma,$$

where $n'' - n'$ and $n_F'' - n_F'$ are each small compared to the quantum numbers involved.

Since there are no limitations on the values of $n_F'' - n_F'$, the radiation emitted contains both the fundamental frequencies $\omega \pm \sigma$ as well as their harmonics. The number of components is consequently quite large when compared with that obtained in the Zeeman effect.

The more rigorous discussion of the Stark effect by E. Schroedinger,[2] using the methods of wave mechanics, does not substantially alter the nature of the conclusion deduced by the earlier investigators. In terms of the more recent theory we must regard the splitting up in the electric field as due primarily to a separation of the center of gravity of the electric charge distribution from the position of the positively charged nucleus (as indicated in Fig. 12.8) which results in the creation of an *electric dipole moment*. The magnitude of this moment depends upon the field and upon the orientation of the orbit, that is, upon the direction of the angular momentum J, with respect to the field. There results a *space quantization* into levels with quantum numbers J, $J - 1$, $\cdots$, $- J$. However, there is an important difference between the number of levels obtained in the Zeeman and Stark effects for the same value of J. Since the electric dipole moment is not reversed by a change from $+ J$ to $- J$, the num-

[1] E. Buchwald, *op. cit.*, p. 73.

[2] *Ann. Physik*, **80**, 437 (1926).

ber of components for a given value of J is $J + \frac{1}{2}$ or $J + 1$, according as J is half integral or integral.[1]

As in the case of magnetic fields, the LS coupling is destroyed in very strong electrostatic fields and consequently the nature of the line pattern alters materially.[2]

13. ELECTRON CONFIGURATION IN ATOMS AND PERIODIC SYSTEM OF THE ELEMENTS

(1) **Pauli Exclusion Principle:** As stated in a previous section, the Schroedinger differential equation for the hydrogen atom leads to a series of discrete energy states which involve only the total quantum number n. Associated with each of these energy states we find a number of eigenfunctions which are characterized by the two subsidiary quantum numbers, l and m. While l corresponds to the angular momentum due to the motion of the electron, the number m indicates a possible orientation of this angular momentum (regarded as a vector) in a magnetic field. Thus l and m designate for a single electron the same magnitudes as L and M for a spectroscopic term which arises from the interaction of two or more electrons.

Since $l = n, n - 1, \cdots, 0$, and $m = l, l - 1, \cdots, -l$, there are associated with any given value of l, $(2l + 1)$ values of m.

If in addition to these quantum numbers we bring in the concept of electron spin, then it is necessary to assign to the latter a spin quantum number, s, which may have one of the two values $s = \pm \frac{1}{2}$, and as follows from the discussion of the Paschen-Back effect, this gives rise to two possible states in a magnetic field which we shall designate by the quantum number $m_s (= \pm \frac{1}{2})$. (Thus m_s corresponds to the quantum number M_S for a spectroscopic term, and by analogy the symbol m_l is often used instead of m.)

In a magnetic field, two electrons having the same values of n, l and m but different values of m_s, will differ slightly in energy because of the different modes of interaction with the field of the magnetic moments arising from opposite directions of spin. It follows from these considerations that for an electron of quantum number l, the maximum number of energy levels in a magnetic field is $2(2l + 1)$, and to each of these levels we can assign a different pair of values of the two quantum numbers m and m_s.

Now, according to Pauli we can never have in any atomic system more electrons than there are possible energy states for a given value of n. Furthermore *in any one atom there cannot exist two electrons having the same set of values of the four quantum numbers n, l, m and m_s.*

That is, if for two electrons (designated by 1 and 2), $n_1 = n_2$, $l_1 = l_2$ and $m_1 = m_2$, then m_s for these electrons must have the values $+ \frac{1}{2}$ and $- \frac{1}{2}$.

While *Pauli's Exclusion Principle* has not been deduced from any theoretical

---

[1] Ref. G. H., pp. 115–116.

[2] Recent investigations on the Stark effect have been reviewed comprehensively by H. Verleger, *Ergebn. exakt. Naturwiss.*, **18**, 99 (1939).

considerations, its validity is confirmed by all spectroscopic observations, especially those on the nature of the spectral terms for atoms with more than one valence electron.

(2) **Stoner's and Main-Smith's Scheme of Electronic Configuration of Atoms**: Even before the announcement by Pauli of his principle, E. C. Stoner [1] and J. D. Main-Smith [2] made implicit use of the same idea for developing a scheme of electron configuration of atoms which accounts for the observations on the periodic arrangement of the elements. Recognizing, in view of the observations on the Zeeman effect, that the maximum number of levels for an electron of quantum number l, is $2(2l + 1)$, they postulated that the latter number must also represent *the maximum number of electrons of that type which can occur in an atomic system.*

Thus if we consider the different possible levels for values of n ranging from 1 to 4 we obtain the results shown in Table 13.1. It will be observed that for any level of type $s(l = 0)$, the maximum number of electrons is 2, while for levels of type p, d and f (corresponding to $l = 1$, 2 and 3 respectively, the maximum numbers of electrons are 6, 10 and 14 respectively.

TABLE 13.1

n	Value of l	Spectral Designation	Number of Levels in Magnetic Field
1	0	$1s$	2
2	0	$2s$	2
	1	$2p$	6
3	0	$3s$	2
	1	$3p$	6
	2	$3d$	10
4	0	$4s$	2
	1	$4p$	6
	2	$4d$	10
	3	$4f$	14

On this basis it is possible to deduce electron configurations for the different atoms as we proceed from hydrogen to elements of higher atomic number.

The electron in the atom of hydrogen is of type $1s$. To form an atom of helium, a second electron of same type is added (and, of course, the nuclear charge is increased by one unit of positive electricity). In accordance with Pauli's principle the two electrons in helium must possess opposite spins. This completes the group of quantum number $n = 1$, and in the process of building

[1] *Phil. Mag.*, **48**, 719 (1924).

[2] Chemistry and Atomic Structure, D. Van Nostrand Co., New York (1924).

up of atoms by adding electrons, the group $n = 1$ forms the K shell, the diameter of which varies approximately inversely as the nuclear charge.

With the addition of a third electron we begin to form the group for $n = 2$, and the electrons in lithium and beryllium are of type 2s. Consequently the electronic configuration for beryllium is denoted by the expression $1s^2 2s^2$, in which the exponent indicates the number of electrons of the given type. The next electron has to be of type 2p. Corresponding to $l = 1$, there are three eigenfunctions, associated respectively with the magnetic quantum numbers $m = +1$, 0 and -1. Following the procedure used by L. Pauling [1] these three functions will be designated as p_x, p_z and p_y. Pauling has also introduced the term *orbital* to designate these eigenfunctions, which reminds us, as it were, of the intimate connection between the wave mechanics representations and the more simple models used by Bohr. Again, because of possible differences in electron spin, it is possible to have two electrons of the same orbital type. Furthermore, according to Pauling, "when there are several orbitals of the same energy available, such as $2p_x$, $2p_y$, $2p_z$, they tend not to pair with one another, but instead to occupy different orbitals, keeping their spins parallel. For example, the normal nitrogen atom has the configuration $1s^2 2s^2 2p_x 2p_y 2p_z$, the three 2p electrons remaining unpaired." In neon this pairing is completed and at the same time all possible orbitals for $n = 2$ are occupied. Consequently this completes the so-called L-shell. (See Table 13.2.)

The same procedure is repeated with electrons of quantum number $n = 3$, as we pass from sodium to argon, and the electron configuration of the latter is $1s^2 2s^2 2p^6 3s^2 3p^6$. In the case of potassium, the similarity with lithium and sodium leads to the conclusion that the added electron must be of the 4s type. Much more important, however, in the case of this and other atoms is a criterion which may be stated as follows: During the process of formation of atoms by addition of successive electrons the *last bound electron* is *always of that orbital type for which the energy of the atomic system is a minimum.* Thus in the case of potassium, observations on the relative energies of the different spectral terms show that an electron in a 3d state has a higher energy value (less binding energy) than in a 4s state. The same holds true for calcium (At. No., 20), but in the case of the next element, scandium, the energy in a 3d state is lower than that in a 4p level (since the 4s state is already occupied by two electrons). Consequently we begin, with this element, to fill up the 3d group of orbitals, for which the maximum number of electrons is 10. As shown in Table 13.2, the completion of this group occurs in copper (At. No., 29). With the addition of 8 electrons in the N-shell of configuration $4s^2 4p^6$ we obtain krypton, the fourth member of Group 0.

Proceeding to still larger atomic numbers, we obtain a very natural explanation for the occurrence of the two long periods K-Ar and Rb-Xe, and for the occurrence of the rare earth group Ce-Lu. It will be observed that while all

[1] L. Pauling, The Nature of the Chemical Bond, Cornell University Press, Ithaca, N. Y. (1939) (Ref. L. P.) See Table 10.1.

TABLE 13.2

Element	Z	K	L		M			N		Ground Term	V_i
		$1s$	$2s$	$2p$	$3s$	$3p$	$3d$	$4s$	$4p$		
H	1	1								$^2S_{1/2}$	13.595
He	2	2								$^1S_0$	24.58
Li	3	2	1							$^2S_{1/2}$	5.39
Be	4	2	2							$^1S_0$	9.32
B	5	2	2	1						$^2P_{1/2}$	8.32
C	6	2	2	2						$^3P_0$	11.26
N	7	2	2	3						$^4S_{3/2}$	14.55
O	8	2	2	4						$^3P_2$	13.61
F	9	2	2	5						$^2P_{3/2}$	17.42
Ne	10	2	2	6						$^1S_0$	21.56
Na	11				1					$^2S_{1/2}$	5.14
Mg	12				2					$^1S_0$	7.64
Al	13				2	1				$^2P_{1/2}$	5.99
Si	14	Neon Core			2	2				$^3P_0$	8.15
P	15	(10)			2	3				$^4S_{3/2}$	10.95
S	16				2	4				$^3P_2$	10.35
Cl	17				2	5				$^2P_{3/2}$	13.01
A	18				2	6				$^1S_0$	15.76
K	19							1		$^2S_{1/2}$	4.34
Ca	20							2		$^1S_0$	6.11
Sc	21						1	2		$^2D_{3/2}$	~6.7
Ti	22						2	2		$^3F_2$	6.83
V	23	Argon Core					3	2		$^4F_{3/2}$	6.74
Cr	24	(18)					5	1		$^7S_3$	6.76
Mn	25						5	2		$^6S_{5/2}$	7.43
Fe	26						6	2		$^5D_4$	7.87
Co	27						7	2		$^4F_{9/2}$	7.84
Ni	28						8	2		$^3F_4$	7.63
Cu	29						10	1		$^2S_{1/2}$	7.72
Zn	30							2		$^1S_0$	9.39
Ga	31							2	1	$^2P_{1/2}$	6.00
Ge	32							2	2	$^3P_0$	8.13
As	33	Cu$^+$ Core						2	3	$^4S_{3/2}$	10.5(H)
Se	34	(28)						2	4	$^3P_2$	9.75
Br	35							2	5	$^2P_{3/2}$	11.84
Kr	36							2	6	$^1S_0$	14.00

TABLE 13.2 (*Continued*)

Element	Z	Number in Inner Shells	N 4d	N 4f	O 5s	O 5p	P 5d	P 6s	Ground Term	V_i
Rb	37				1				$^2S_{1/2}$	4.18
Sr	38				2				$^1S_0$	5.69
Y	39		1		2				$^2D_{3/2}$	~6.5
Zr	40		2		2				$^3F_2$	6.95
Cb	41	Krypton Core (36)	4		1				$^6D_{1/2}$	—
Mo	42		5		1				$^7S_3$	7.38
Ma	43		6		1				$^6D_{9/2}$	—
Ru	44		7		1				$^5F_5$	(7.7)
Rh	45		8		1				$^4F_{9/2}$	7.74
Pd	46		10						$^1S_0$	8.34
Ag	47				1				$^2S_{1/2}$	7.57
Cd	48				2				$^1S_0$	8.99
In	49				2	1			$^2P_{1/2}$	5.80
Sn	50	Palladium Core (46)			2	2			$^3P_0$	7.34
Sb	51				2	3			$^4S_{3/2}$	(8.35)
Te	52				2	4			$^3P_2$	9.00
I	53				2	5			$^2P_{3/2}$	10.6(H)
Xe	54				2	6			$^1S_0$	12.13
Cs	55							1	$^2S_{1/2}$	3.89
Ba	56							2	$^1S_0$	5.21
La	57						1	2	$^2D_{3/2}$	5.6(H)
Ce	58			1			1	2	$^3H_4$	6.56(H)
Pr	59			2			1	2	$^4K_{11/2}$	(5.8)
Nd	60			3			1	2	$^5L_6$	(6.3)
Il	61			4	5s5p "Shell" (8)		1	2	$^6L_{9/2}$	—
Sm	62			5			1	2	$^7K_4$	6.6
Eu	63			6			1	2	$^8H_{3/2}$	5.66(H)
Gd	64	Palladium Core (46)		7			1	2	$^9D_2$	(6.7)
Tb	65			8			1	2	$^8H_{17/2}$	(6.7)
Ds	66			9			1	2	$^7K_{10}$	(6.8)
Ho	67			10			1	2	$^6K_{19/2}$	—
Er	68			11			1	2	$^5L_{10}$	—
Tu	69			12			1	2	$^4K_{17/2}$	—
Yb	70			13			1	2	$^3H_6$	(7.1)
Lu	71			14			1	2	$^2D_{3/2}$	—

← RARE EARTH GROUP →

* According to W. F. Meggers (*J. Opt. Soc. Am.*, **31**, 157 (1941)) the most recent spectroscopic evidence leads to the following electron configurations and ground terms for a number of the rare earth group elements: Nd, f^4s^2, ^5I; Il, f^5s^2, ^6H; Sm, f^6s^2, ^7F; Eu, f^7s^2, ^8S; Ds, $f^{10}s^2$, ^5I; Ho, $f^{11}s^2$, ^4I; Er, $f^{12}s^2$, ^3H; Tu, $f^{13}s^2$, ^2F; Yb, $f^{14}s^2$, ^1S. For the other five elements the configurations and ground terms are as indicated in the table.

TABLE 13.2 (*Continued*)

Element	Z	Number in Inner Shells	O	P			Q	Ground Term	V_i
			5d	6s	6p	6d	7s		
Hf	72		2	2				$^3F_2$	
Ta	73		3	2				$^4F_{3/2}$	
W	74	Lu^{+++} Core	4	2				$^5D_0$	(8.1)
Re	75	(68)	5	2				$^6S_{5/2}$	
Os	76		6	2				$^5D_4$	~8.7
Ir	77		9					$^2D_{5/2}$	~9.2
Pt	78		9	1				$^3D_3$	8.92
Au	79		10	1				$^2S_{1/2}$	9.23
Hg	80			2				$^1S_0$	10.43
Tl	81			2	1			$^2P_{1/2}$	6.10
Pb	82			2	2			$^3P_0$	7.42
Bi	83	Au$^+$ Core		2	3			$^4S_{3/2}$	(7.25)
Po	84	(78)		2	4			$^3P_2$	—
—	85			2	5			$^2P_{3/2}$	—
Rn	86			2	6			$^1S_0$	10.75
—	87						1	$^2S_{1/2}$	—
Ra	88						2	$^1S_0$	5.27
Ac	89	Radon Core				1	2	$^2D_{3/2}$	—
Th	90	(86)				2	2	$^3F_2$	—
Pa	91					3	2	$^4F_{3/2}$	—
U	92					4	2	$^5D_0$	—

these elements are identical with respect to the configuration of the external group of O and P electrons, they differ in the number of electrons in $4f$ states. Furthermore, since it is possible to have at the maximum only 14 electrons of type f, this accounts for the observation that there are that number of elements in the rare earth group.

Table 13.2 gives, besides the electron configuration, the term symbol and ionization potential, as far as known, for each element in the normal or ground state. In a subsequent section there will be discussed the method by which the term symbols have been derived for atoms containing more than one electron in the outer or valence shell. (These electrons are also often designated "optical" electrons as distinguished from the inner electrons which are of importance in the interpretation of X-ray spectra, as shown in the next section.)

The ionization potentials, which will also be discussed in a subsequent section, have been determined in most cases from investigations on the values of spectral terms. This applies especially to elements of the first three groups in the periodic arrangement. In the case of elements with more complex electronic configurations, other methods have been used, wherever possible, to supplement the deductions from spectroscopic data. For instance, the

nature of the resonance lines has been determined by absorption measurements with the vapors, and in some cases, the ionization potential has been determined directly by observing the minimum velocity of electrons required to produce ionization in the vapor.

Moreover extremely significant information on the type of electronic configuration has been obtained from investigations on the nature of spectral terms in enhanced spectra and X-ray spectra. We shall therefore consider in the following section these two classes of observations.

(3) **Enhanced Spectra:** A particularly interesting class of spectra from which significant conclusions have been drawn about the process of building-up of atoms by addition of electrons is that known as "enhanced spectra."

According to the Bohr theory the energy of an atomic system consisting of a nucleus of charge Ze and a single electron is given by

$$E_n = - \frac{RchZ^2}{n^2}, \tag{13.1}$$

where n is the quantum number of the electron.

Bohr utilized this relation to show, as has been mentioned previously, that certain lines previously ascribed to hydrogen actually belong to ionized helium, for which Z is 2. It is evident that for an atomic system from which one electron has been removed, that is, a singly-ionized atom, the force between the "optical" electron and the rest of the atom (or *kernel*) will approximate that between a nucleus of charge $+ 2e$ and an electron, especially for non-penetrating orbits. Thus the spectra of singly-ionized atoms will possess terms in which the Rydberg constant R, obtained for ordinary spectra (those of neutral atoms) is replaced by 2^2R. Now such spectra had been observed and were known as "*spark*" spectra in contradistinction to the more usual "*arc*" spectra.

Bohr's theory, however, led to the conclusion that it should also be possible to observe spectra due to atoms in which two or more electrons have been removed, and for these "*enhanced*" spectra the value of the Rydberg constant would have to be replaced by $4R$, $9R$ or p^2R according as one, two or $(p - 1)$ electrons have been removed from the neutral atom. It has become conventional to designate such a "stripped" atom by the symbol of the element, to which is attached at the lower right hand corner a Roman numeral whose value is equal to that of p. Thus we speak of the spectrum of F_{VII} and signify by this symbol the spectrum emitted by a fluorine atom which has been stripped of *six* external electrons and therefore actually has the same number of valence electrons as the Li atom.

Evidently the first spark spectrum of any element ought to exhibit the same multiplet structures as the arc spectrum of the element preceding it in the periodic table. (Kossel-Sommerfeld's displacement law.) Furthermore, the enhanced spectrum of an element of atomic number Z from which p electrons have been removed should resemble the ordinary spectrum of an element of

atomic number $Z - p$.   (But, of course, the coefficient of the Rydberg constant in the case of the enhanced terms would be $(p + 1)^2$.)

A very interesting illustration of these considerations is furnished by the spectra of the series Na_I, Mg_{II}, Al_{III}, Si_{IV}, which have been investigated by Paschen, Foote and Fowler,[1] and P_V, S_{VI}, and Cl_{VII} investigated by Millikan and Bowen.[2]   All these spectra exhibit doublet levels, but owing to the effect of increasing net nuclear charge, the wave lengths of similar lines (i.e., corresponding to transitions between levels of same spectral designation) become shorter as the number of electrons removed from the atom increases.   Thus Fig. 13.1 [1, 3] shows the "D" lines in the spectra of the first four atoms.
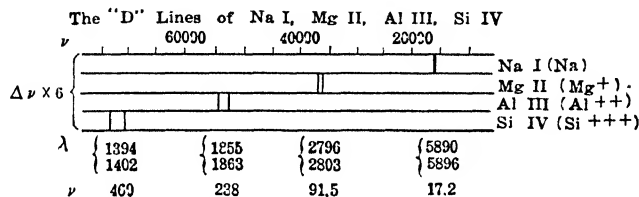
FIG. 13.1.   "D" Lines in Enhanced Spectra of Sodium-Like Atoms

Table 13.3 (from the paper by Fowler) gives a comparison of the lowest series terms for these spectra.   In accordance with equation (13.1) the observed values of $\tilde{\nu}$ have been divided by p^2 where $p - 1$ designates the number of electrons removed from the neutral atom.   The values of $\tilde{\nu}$ for the corresponding levels in H are given at the top.   Here again it is observed that the values for D and F levels are approximately the same as those for similar levels in H, (thus indicating that the corresponding orbits are completely external to the rest of the atom) while owing to the deeper penetration of the s and p orbits the corresponding energy values (as measured by the values of $\tilde{\nu}$) are greater.   Consequently the quantum defect ($\alpha_K = n - n_{eff.}$) decreases as we pass from Na_I to S_{VI}.

TABLE 13.3

COMPARISON OF WAVE NUMBERS OF SERIES TERMS FOR STRIPPED ATOMS Na_I TO S_{VI}

	$3S$	$3P$	$3D$	$4F$
H.	12192.8	12192.8	12192.8	6858.4
Na/1.	41449.0	24475.7	12276.2	6860.4
Mg/4	30316.9	21376.6	12444.3	6866.8
Al/9.	25494.9	19504.0	12611.0	6871.3
Si/16.	22756.8	18272.6	12733.7	6874.2
P/25.	20979.7	17401.9	12811.8	6876.4
S/36.	19729.6	16753.6	12856.6	6878.1

[1] A. Fowler, *Proc. Roy. Soc.*, [A], 103, 722 (1923).

[2] I. S. Bowen and R. A. Millikan, *Phys. Rev.*, 25, 295 (1925).

[3] A. Fowler, *Nature*, 113, 217 (1924).

Millikan and Bowen have also obtained the spectra of the series Li_I to F_{VII} and these show variation in the frequencies of series terms similar to those observed for the series Na_I to Cl_{VII}.

While these spectra all resemble those of the alkali metal group in exhibiting doublet levels, Millikan and Bowen have also found spectra of stripped atoms which resemble the metals of Group II in exhibiting singlet and triplet levels. Such are the series:

$$Be_I, \quad B_{II}, \quad C_{III}, \quad N_{IV}, \quad O_V, \quad F_{VI}$$
$$Mg_I, \quad Al_{II}, \quad Si_{III}, \quad P_{IV}, \quad S_V, \quad Cl_{VI}$$
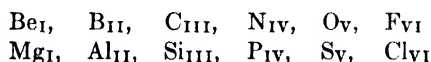
In fact the spectra of all these atoms and a number of others have been obtained in all the various states of enhancement. Thus the spectra of series such as P_I to P_V and Si_I to Si_{IV}, N_I to N_V, have been observed by Millikan and Bowen,[1] while spectra of stripped atoms of the K, Rb and Cs series have been investigated by R. C. Gibbs and H. E. White.[2] Further reference to this topic will be made in the section on isoelectronic sequences.

14. Quantum Numbers for Inner Electrons

(1) **X-ray Levels and Associated Transitions:** In Section 1.5 some of the more elementary aspects of our knowledge of X-ray spectra were presented, such as the observations on the occurrence of K-, L- and M- series of lines and the relations of these series to K-, L- and M-levels. Furthermore, mention was was made of Moseley's observations which led to the concept of atomic number. In the present section we shall consider especially the interpretation of these X-ray levels from the point of view of electron configurations and the relation between X-ray and optical spectra.

From his observations on the wave lengths of $K\alpha$-lines for different elements, Moseley deduced the empirical relation

$$\sqrt{\nu} = a(Z - \sigma_0),$$

where ν = frequency, and a and σ_0 are constants. A similar law has been found to be valid, to a first approximation, for other members of the K-series, as illustrated in Fig. 1.12 by the plot of $\sqrt{\tilde{\nu}/R}$ against Z, where R denotes the Rydberg constant. For the range $Z = 20$ to $Z = 30$, the Moseley relation for the $K\alpha$-line has the form

$$\sqrt{\tilde{\nu}/R} = 0.874(Z - 1.13), \tag{14.1a}$$

which may be expressed in the form,

$$\tilde{\nu}/R = 0.764(Z - 1.13)^2. \tag{14.1b}$$

[1] *Phys. Rev.*, **23**, (1924); **26**, 310 (1925); **27**, 144 (1926); **28**, 256 (1926); **29**, 231, 510 (1927).

[2] *Proc. Nat. Acad. Sci.*, **12**, 448, 551 (1926); **13**, 525 (1927); *Phys. Rev.*, **29**, 426, 655 (1927), **33**, 157 (1929). See also Ref. H. E. W., Chap. XVII.

Now let us consider as a possible interpretation of this line that it arises from a transition between two levels corresponding to $n = 2$ and $n = 1$. As follows from Table 13.2, the electrons in these states are much closer to the nucleus than electrons of higher quantum number which correspond to the valence electrons. Owing to the presence of these other electrons, the nuclear charge effective on the inner electrons will be less than Z, say $Z - \sigma$, where σ may be regarded as a "screening constant." On the basis of either the simple Bohr theory of the hydrogen-like atom, or wave mechanics, we would expect a frequency relation, for the transition $n = 2$ to $n = 1$, of the form:

$$\bar{\nu}/R = (Z - \sigma)^2 \left\{ \frac{1}{1^2} - \frac{1}{2^2} \right\}$$

$$= 0.75(Z - \sigma)^2. \tag{14.2}$$

The close agreement between this result and the empirical equation (14.1*b*) leads to the conclusion that the K-levels correspond to the spectroscopic 1*s*-states. As a further confirmation of this view it has been shown by Millikan that the limiting frequency in the Lyman series forms an extension of the plot for the frequencies of $K\alpha$-lines as a function of Z.

As mentioned in Section 1(5) an investigation of X-ray spectra has led to evidence for the existence of not only K-levels but also L- and M- levels which correspond to higher energy states (lower binding energy) for the electrons, while in the case of elements of high atomic number we find levels which are associated with still lower binding energies. These are designated, in order of decreasing binding energy as N-, O- and P-levels. The evidence for the existence of these levels is obtained, as pointed out already, from X-ray absorption spectra and by application of Einstein's law giving the relation between maximum frequency of radiation emitted and voltage applied. In this manner we obtain the following "picture" of the X-ray levels and mode of origin of X-ray spectral lines.

In the process of building up atoms by adding electrons, those of quantum number $n = 1$, will be closer, on the whole, to the nucleus than those corresponding to $n = 2$, while those of still higher quantum numbers will be further out. We can thus conceive of the electrons as forming "shells," and since the K-radiations have the highest frequencies we must regard these as produced by the removal of an electron from the K-shell, followed by the spontaneous transfer of an electron from one of the outer shells to the K-shell. The L-radiation is produced in a similar manner by the transfer of electrons from other shells such as those designated M, N, etc. to the L-shell, from which an electron has been removed. Since this shell is further out from the nucleus, the amount of energy required to remove an electron from this shell is less than that required to remove an electron from the K-shell. Consequently, the frequencies of the L-radiations, which correspond to transitions from outer shells to the L-shell are lower than those of the K-radiations.

We thus obtain a qualitative representation of the origin of X-rays such as that shown in Fig. 14.1.[1] The process of excitation is represented dia-
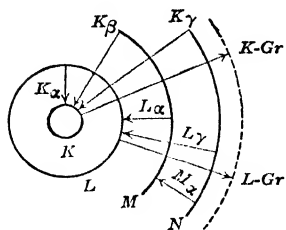
grammatically by the arrows that point outwards. They terminate on a circle, indicated by dashes, and are labelled K-Gr (K-limit) and L-Gr (L-limit), corresponding to frequencies ν_K and ν_L which represent the limiting values for the respective series. Similar frequencies, ν_M, ν_N, etc., are obtained which are associated with the M-, N-levels, etc. This concept of the origin of the different series of X-radiations has been presented already in

Fig. 14.1. Schematic Representation of Origin of Different Types of X-Rays

Section 1.5, and illustrated by Fig. 1.13.

In order to obtain from a given target *any* one of the K-lines, the voltage applied to the X-ray tube must be increased to the value V given by the Einstein relation

$$Ve = h\nu_K, \tag{14.3}$$

for which the obvious explanation is that in order to obtain any K-radiation at all an electron must first be removed from the K-shell.

Similarly, in order to excite any line of the L-series, it is necessary to apply a voltage greater than that determined, in accordance with Einstein's law, by the value of ν_L. Actually, there are three L-levels, and by carefully regulating the voltage it is possible to obtain radiations of the L_{III}-series, but not those of the L_{II}-series. Thus, in the case of tungsten the three excitation limits are:

$$
\begin{array}{lll}
L_{III}\text{-limit} & V = 10.2 \text{ kilovolts} \\
L_{II}\text{-limit} & V = 11.6 & \text{``} \\
L_{I}\text{-limit} & V = 12.0 & \text{``}
\end{array}
$$

In Fig. 14.2 are shown Moseley plots ($\sqrt{\bar{\nu}/R}$ versus Z) for the different levels.[2] Each plot can be represented to a first approximation by a linear relation of the form

$$\sqrt{\frac{\bar{\nu}}{R}} = \frac{Z - \sigma}{n}, \tag{14.4}$$

where σ represents, as in equation (14.2), a screening constant, and hence $Z - \sigma$ is the *effective nuclear charge*. The fact that these plots lead to the values $n = 1$, 2, 3 etc., for the K-, L-, M-levels and so forth, respectively, leads to the schematic illustration of the process of emission of X-rays which is illustrated in Fig. 14.3.[3]

[1] A. Sommerfeld, *op. cit.*, p. 248.

[2] Bohr and Coster, *Z. Physik*, 12, 342 (1923).

[3] A. Sommerfeld, *op. cit.*, p. 250; Atomic Structure and Spectral Lines, E. P. Dutton and Co., New York, 1923, p. 146.

"This diagram," as Sommerfeld describes it, "has an advantage in that it takes more account of the quantitative aspect of the phenomenon. In it we
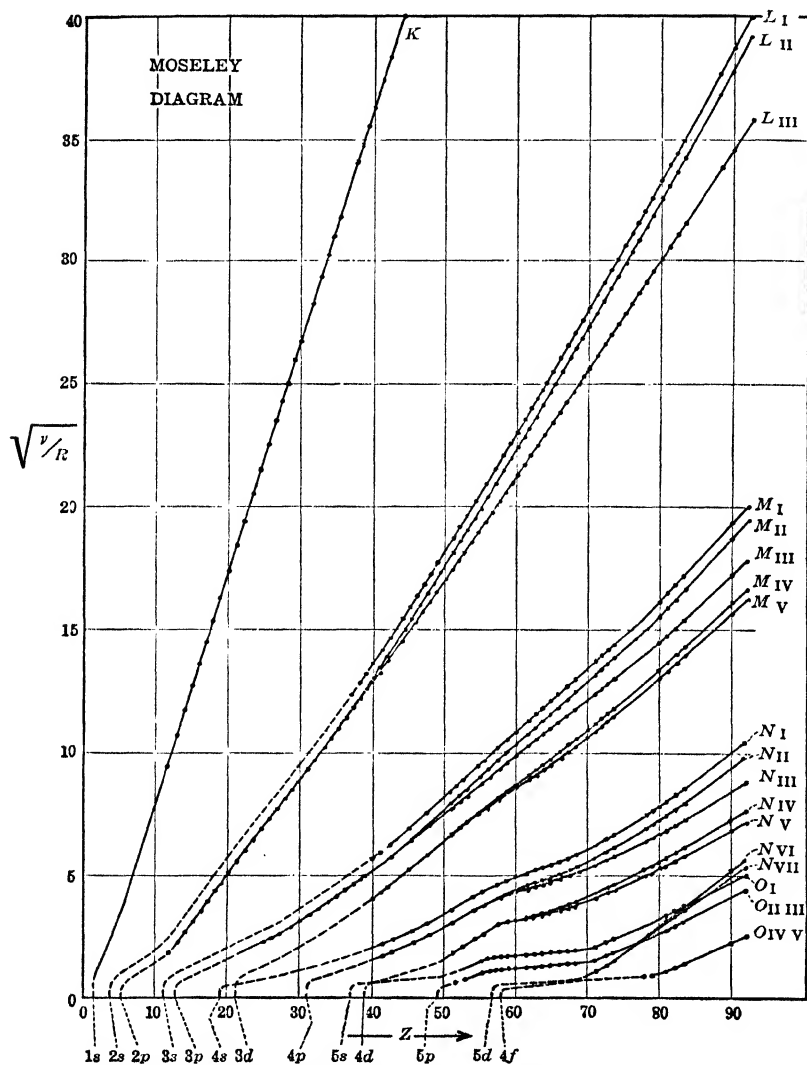

Fig. 14.2. Moseley Plots for X-Ray Levels. (In these plots ν denotes the wave number)

visualize the various shells not by their relative positions in the atom, but by their relative energy-differences. Thus we draw a succession of energy-steps such that the difference in height between two steps gives the energy that is

liberated when an electron drops from the higher to the lower step (orbit). The lowest step bears the sign K, the next L, and so forth. The energy level of the nucleus is to be considered at $-\infty$. The highest dotted limit of the steps corresponds to the periphery of the atom. The quantitative drawing of the picture leads us to assign to the successive steps K, L, M, N, etc., the series of integral 'quantum numbers' 1, 2, 3, 4, etc., in such a way that the position of each step below the highest level is, at least to a certain degree of approximation, proportional to
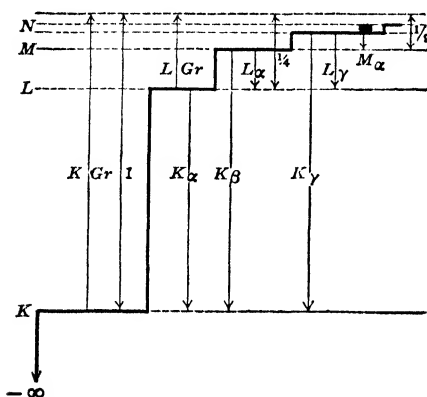
Fig. 14.3.   Energy Levels for Excitation
of X-Rays

$$\frac{1}{1^2}, \quad \frac{1}{2^2}, \quad \frac{1}{3^2}, \quad \frac{1}{4^2}, \quad \cdots .$$

Accordingly we make the height of the steps in the figure decrease, from the bottom upwards, in the manner indicated by the differences in height 1, $\frac{1}{4}$, $\frac{1}{9}$, $\cdots$ written at the side (on the right). Moreover, we again draw the arrows $K\alpha$, $K\beta$, $\cdots$, $L\alpha$, $\cdots$ that correspond to the various possibilities of energy-emission, and the arrows K-Gr, L-Gr, which correspond to the various kinds of energy absorption." These arrows thus indicate the limits of the K and L series.

From these considerations it is evident that X-ray spectra are to be considered as indicating the process by which an atomic system undergoes reorganization after a disturbance of the electrons constituting the kernel (that is that portion of the atom which remains after removal of the valence or outer electrons), just as optical spectra represent the reorganization process after a disturbance in the valence shell.

(2) **Doublet Levels in X-ray and Optical Spectra:** For the K-level with total quantum number $n = 1$ the only possible value of l is 0, that is, this level corresponds to the optical $1s$ state, and in accordance with Pauli's principle there can be only two electrons in the atom of this type. Thus the K-electrons are of the same type as the two electrons in the helium atom, only the binding energy for the former is much greater, because the field in which they move is due to a positive charge of magnitude $(Z - \sigma)e$ instead of $2e$.

In the case of L- and M-levels, Fig. 14.2 indicates the presence of multiplet levels, and the problem arises regarding the assignment of subsidiary quantum numbers l and j. The solution of this problem is based upon the observation that certain empirical relations apply to the frequency differences between the components of the multiplet levels.

As shown in the figure, the value of $\Delta\bar{\nu}$, the difference in wave numbers for

the levels L_{II} and L_{III} increases with Z. The variation in $\Delta\tilde{\nu}_L$ (the subscript indicating that it is the difference for the L-levels) with Z may be represented very satisfactorily by a relation of the form

$$\Delta\tilde{\nu}_L = 0.365(Z - \sigma_1)^4 \text{ cm.}^{-1}, \qquad (14.5)$$

where σ_1 is, again, a screening constant.

Similarly the value of $\Delta\tilde{\nu}$ for the M_{II} and M_{III} levels may be represented fairly accurately by the relation

$$\Delta\tilde{\nu}_M = 0.108(Z - \sigma_2)^4 \text{ cm.}^{-1}, \qquad (14.6)$$

where σ_2 is not the same as σ_1.

Now relations of this form were derived by A. Sommerfeld for the difference in energy of two orbits having identical values of n but different values of the azimuthal quantum number k. The considerations on which these relations were deduced may be stated briefly as follows:

According to the theory of relativity, the mass of an electron increases with the velocity. In an elliptic orbit the velocity of the electron is a maximum at perihelion (that is the point at which the radius vector is a minimum) and a minimum at aphelion (maximum distance from the focus.) Because of this the energy of the system should be given, to a first approximation in powers of $\alpha^2(Z - \sigma)^2$, by a relation of the form,

$$E_{nk} = -\frac{2\pi^2(Z - \sigma)^2 e^4 m_0}{n^2 h^2}\left[1 + \frac{\alpha^2(Z - \sigma)^2}{n}\left(\frac{1}{k} - \frac{3}{4n}\right)\right], \qquad (14.7)$$

where $\alpha(= 2\pi e^2/hc)$ is known as the "fine-structure" constant, while $Z - \sigma$ is the *effective* nuclear charge. Hence the *difference in wave number* for two states having the same value of n, but different values of k, should be given by the relation

$$\Delta\tilde{\nu} = \frac{R(Z - \sigma)^4\alpha^2}{n^3}\left(\frac{1}{k_1} - \frac{1}{k_2}\right). \qquad (14.8)$$

For $n = 2$, the only possible values of k are 1 and 2. Hence

$$\Delta\tilde{\nu}_{12} = \frac{R(Z - \sigma)^4\alpha^2}{2^3} \cdot \frac{1}{2} = 0.365(Z - \sigma)^4 \text{ cm.}^{-1}. \qquad (14.9)$$

For $n = 3$, the difference for $k = 1$ and $k = 2$ is given by the relation

$$\Delta\tilde{\nu}_{12} = 0.108(Z - \sigma)^4 \text{ cm.}^{-1}, \qquad (14.10)$$

and for $k = 2$ and $k = 3$, by the relation

$$\Delta\tilde{\nu}_{23} = 0.036(Z - \sigma)^4 \text{ cm.}^{-1}. \qquad (14.11)$$

On the basis of this theory Sommerfeld was able to account quantitatively for the so-called fine structure (see following section) of the lines in the spectra of hydrogen and ionized helium.

In view of the similarity between equations (14.9) and (14.5) on the one hand, and (14.10) and (14.6) on the other, it was therefore concluded that L_{II} represented an orbit for which $k = 1$, and L_{III}, one for which $k = 2$, and similarly for M_{II} and M_{III}. These pairs of levels were therefore designated as "relativity" or *regular* doublet levels.

On the other hand, the levels $L_I L_{II}$, $M_I M_{II}$ are known as the *irregular* doublet levels, or "screening" doublets. For these pairs of levels the values of the differences $\sqrt{\nu_{L_I}} - \sqrt{\nu_{L_{II}}}$ and $\sqrt{\nu_{M_I}} - \sqrt{\nu_{M_{II}}}$ increase, as was shown by G. Hertz,[1] only slightly with increase in Z, as is evident from Fig. 14.2. According to Hertz this constant difference in $\sqrt{\bar{\nu}}$ could be accounted for, on the basis of Moseley's law (see equation (14.4)) by a difference in the value of σ for each component of the pair of levels.

Now in the case of the alkali metals the difference between the $S_{1/2}$ and $P_{1/2}$ levels was accounted for by Bohr as due to a difference in orbital shape and the consequent *difference in penetration* of the two orbits, while the much smaller difference between the two P-levels was interpreted as due to different *orientations* of the orbits. On the basis of Sommerfeld's theory, the $S_{1/2}$ and $P_{1/2}$ levels ought to form a relativity doublet. But the actual difference between these terms is considerably greater than can be accounted for on the basis of equation (14.5) or (14.6). Thus there existed two different explanations: one for the fine structure of H, He$^+$ and X-ray regular doublets, the other for optical doublets in the alkali metals.

In 1924 Bowen and Millikan [2] showed, however, that for stripped atoms of Li- and Na-like electronic configurations the difference in energy between the $P_{1/2}$ and $P_{3/2}$ terms [*] varies with the atomic number in precisely the same manner as the regular doublet difference in X-ray spectra.

Table 14.1 shows how well their observations agree with the values of $\Delta\bar{\nu}$ calculated by means of equations (14.5) and (14.6). The data in the right-hand column show the application of the irregular doublet law to the $S_{1/2}$ and $P_{1/2}$ levels

It was thus established that the X-ray levels L_{II} and L_{III} are analogous to the optical levels $2P_{1/2}$ and $2P_{3/2}$ respectively, and that M_{II} and M_{III} correspond similarly to the $3P_{1/2}$ and $3P_{3/2}$ levels. This analogy has been found to extend, as shown in Table 14.2, over the whole range of X-ray and optical levels.

Irregular doublet levels are shown bracketed on the left-hand side, while regular or relativity doublet levels are bracketed on the right.

These investigations therefore showed that the following three laws of X-ray spectra could be extended into the field of optical spectroscopy:

[1] *Z. Physik*, **3**, 19 (1920).

[2] *Phys. Rev.*, **24**, 209 (1924); **25**, 295 (1925); **26**, 150 (1925); **27**, 144 (1926).

[*] At that time these levels were designated as p_2 and p_1 respectively.

TABLE 14.1

	$2P_{1/2} - 2P_{3/2}$			$2S_{1/2} - 2P_{1/2}$	
	$\Delta\bar{\nu}$	$\sqrt[4]{\Delta\bar{\nu}/.365}$	σ_2	$\Delta\bar{\nu}$	$\sqrt{\bar{\nu}_S} - \sqrt{\bar{\nu}_P}$
Li$_I$	0.34	0.981	2.019	14903.8	39.470
Be$_{II}$... ...	6.61	2.063	1.937	31927.6	44.297
B$_{III}$...	34.4	3.116	1.884	48358.7	45.594
C$_{IV}$ . .	107.4	4.142	1.858	64481.2	46.068
N$_V$	259.1	5.162	1.939	80455.1	46.276
O$_{VI}$ . . .	533.8	6.184	1.816	96367.8	

	$3P_{1/2} - 3P_{3/2}$			$3S_{1/2} - 3P_{1/2}$	
	$\Delta\bar{\nu}$	$\sqrt[4]{\Delta\bar{\nu}/.108}$	σ_2	$\Delta\bar{\nu}$	$\sqrt{\bar{\nu}_S} - \sqrt{\bar{\nu}_P}$
Na$_I$..	17.18	3.550	7.450	16956.17	47.09
Mg$_{II}$	91.55	5.394	6.606	35669.42	55.67
Al$_{III}$	234.00	6.820	6.180	53681.53	59.76
Si$_{VI}$	461.84	8.084	5.916	71285.49	62.28
P$_V$ . . .	794.82	9.259	5.741	88649.42	64.12
S$_{VI}$.	1267.10	10.404	5.596	105866.04	65.52
Cl$_{VII}$ . .	1889.5	11.496	5.504	123001.23	

(1) The Sommerfeld law [1] of regular or relativistic doublets:

$$\Delta\bar{\nu} = \frac{\alpha^2 R(Z - \sigma_2)^4}{n^3(l + 1)}, \qquad (14.12)$$

where σ_2 is a screening constant, and the smallest value of $l(= k - 1)$ is 1.

TABLE 14.2

ANALOGOUS LEVELS

X-ray Level	Optical Level	X-ray Level	Optical Level
K	$1S_{1/2}$	$\{N_I$	$4S_{1/2}$
$\{L_I$	$2S_{1/2}$	$\{N_{II}\}$	$4P_{1/2}$
$\{L_{II}\}$	$2P_{1/2}$	$\{N_{III}\}$	$4P_{3/2}$
$L_{III}\}$	$2P_{3/2}$	$\{N_{IV}\}$	$4D_{3/2}$
$\{M_I$	$3S$	$\{N_V\}$	$4D_{5/2}$
$\{M_{II}\}$	$3P_{1/2}$	$\{N_{VI}\}$	$4F_{5/2}$
$\{M_{III}\}$	$3P_{3/2}$	$N_{VII}\}$	$4F_{7/2}$
$\{M_{IV}\}$	$3D_{3/2}$	$\{O_I$	$5S_{1/2}$
M_V $\}$	$3D_{5/2}$	$\{O_{II}\}$	$5P_{1/2}$
		$O_{III}\}$	$5P_{3/2}$

[1] See also A. Landé, *Z. Physik*, **25**, 46 (1925). He showed that this law applied to the successive doublet levels in the series for the normal alkali spectra.

(2) The irregular or screening doublet law of Hertz: $\Delta(\sqrt{\bar{\nu}})$ is independent of Z.

(3) The Moseley law

$$\sqrt{\frac{\bar{\nu}}{R}} = \frac{(Z - \sigma_1)}{n}, \qquad (14.4)$$

where σ_1 is a screening constant which does not necessarily have the same value as σ_2.

The application of these laws is best illustrated by the Moseley diagram for sodium-like atoms shown in Fig. 14.4 which is taken from a paper by Bowen
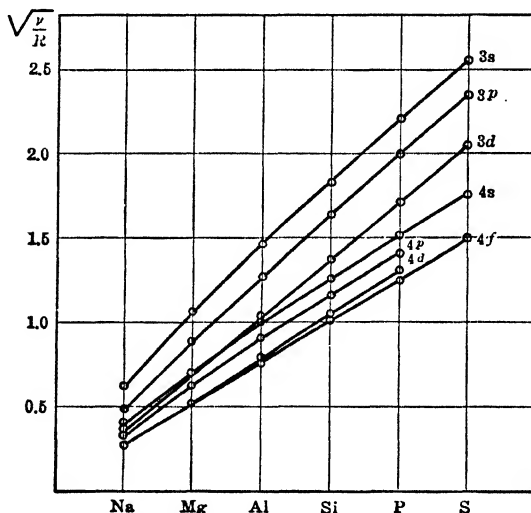
Fig. 14.4.   Moseley Plots for Sodium-Like Atoms

and Millikan.[1] The Moseley law is exhibited in the linearity of the different plots, and the irregular doublet law in the parallelism between $3s$, $3p$ and $3d$ lines. The regular doublet law is not illustrated because the separation between two p- or d-levels is so small that it cannot be shown on the scale used in the diagram.

As is shown in Table 14.1 the value of the screening constant derived by application of (14.12) is approximately 2 for the Li_I series, which corresponds to the number of electrons in the helium or K-shell and therefore represents the residual number of electrons after removal of the L-electrons. In the case of the Na_I series, the value of σ_2 is approximately 6, instead of the expected value 10, which is interpreted as due to a penetration of the $3p$ orbit within the L-shell, and indeed when σ_2 is calculated from the doublet separa-

tions $3D_{3/2} - 3D_{1/2}$ and $4F_{5/2} - 4F_{3/2}$, or from the Moseley plots for these levels the value obtained is close to 10.

These results led Millikan and Bowen [1] to point out the evident inconsistency in assignment of azimuthal quantum numbers to the L_{II} and L_{III} levels as compared with the values used for the $P_{1/2}$ and $P_{3/2}$ levels, and the following quotation from their paper is of special interest in view of the solution which was finally arrived at and which has provided a satisfactory interpretation of the observations.

"The only way," they remark, "in which it appears to be possible to avoid the foregoing serious difficulites is to throw overboard altogether the relativity explanation of the 'relativity doublet' and to assume that the amazing success of this relativity formula in predicting the correct numerical values of σ is not due at all to differences in the shapes of elliptical and circular orbits, as postulated by the relativity theory of doublet separations, but that there is *some other cause which by mere chance leads exactly to this* relativity formula without actually necessitating relativity conceptions."

It is one of the most striking incidents in the history of physics that within a little over a year after these remarks were published "Uhlenbeck and Goudsmit found in the *assumption of the spinning electron* another cause of the fine structure which followed exactly the same law in all respects as the relativity cause." [2]

On the basis of the new mechanics, W. Heisenberg and P. Jordan [3] derived a relation for the energy of a doublet level of the form:

$$- E_{n,l,j} = W_{n,l,j} = \frac{Rch(Z - \sigma_1)^2}{n^2} + \frac{\alpha^2 Rch(Z - \sigma_2)^4}{n^3}\left(\frac{1}{l + \frac{1}{2}} - \frac{3}{4n}\right)$$
$$- \frac{\alpha^2 Rch(Z - \sigma_2)^4}{n^3}\left\{\frac{j(j + 1) - l(l + 1) - s(s + 1)}{2l(l + \frac{1}{2})(l + 1)}\right\}, \quad (14.13)\,[4]$$

where n, l, j are the quantum numbers for the state (j replacing J in the case of terms due to single electrons). The second term on the right-hand side of the equation gives the correction due to *relativity*, and the last term that due to *spin-orbit interaction*. From this equation the following consequences are readily deduced:

(1) For two states having the same values of $Z - \sigma_1$ and $Z - \sigma_2$ and j, but values of l differing by 1 (as e.g., $S_{1/2}$ and $P_{1/2}$ or $P_{3/2}$ and $D_{3/2}$), the *value of the energy is exactly the same*, and is given by the relation

$$- E_{n,l,j} = W_{n,l,j}$$
$$= \frac{Rch(Z - \sigma_1)^2}{n^2} + \frac{\alpha^2 Rch(Z - \sigma_2)^4}{n^3}\left\{\frac{1}{j + \frac{1}{2}} - \frac{3}{4n}\right\}. \quad (14.14)$$

[1] *Phys. Rev.*, **24**, 223 (1924).

[2] R. A. Millikan, *Proc. Am. Phil. Soc.*, **66**, 211 (1927). This paper entitled "Recent Developments in Spectroscopy" contains an excellent review of the subject matter of this section.

[3] *Z. Physik*, **37**, 263 (1926).

[4] This relation is derived in Section 15(7).

In this case, as is evident from Table 11.1, the values of l for the two levels are $l_1 = j + \frac{1}{2}$; $l_2 = j - \frac{1}{2}$. As a matter of fact, the value of $Z - \sigma_1$ is the same for two such levels only in the case of H and He$^+$. For all other atoms, owing to differences in penetration of the orbits, the values of $Z - \sigma_1$ vary with l. If we denote the screening constants corresponding to l_1 and l_2 by σ_{11} and σ_{12} respectively, it follows from equation (14.14) that to a first approximation,

$$\sqrt{\frac{\bar{\nu}_1}{R}} - \sqrt{\frac{\bar{\nu}_2}{R}} = \frac{1}{n}(\sigma_{12} - \sigma_{11}). \tag{14.15}$$

Hence, for two levels arising from a single electron, and having the same value of j, but values of l differing by 1, the *irregular doublet law* must be valid. Furthermore, it also follows from (14.14) that for two such levels

$$\bar{\nu}_1 - \bar{\nu}_2 = R\,\frac{2Z(\sigma_{12} - \sigma_{11}) + (\sigma_{11}^2 - \sigma_{12}^2)}{n^2}. \tag{14.16}$$

That is, the *difference in wave numbers for similar pairs of levels must vary linearly with the nuclear charge*. This represents another method of stating the relation for irregular doublets, and may be illustrated by referring to the data in Table 14.1 for the pairs of levels $2S_{1/2}$, $2P_{1/2}$ and $3S_{1/2}$, $3P_{1/2}$ in lithium-like and sodium-like stripped atoms.

The validity of the linear relation between the values of $\Delta\bar{\nu}$ for each of these pairs of levels and Z in the sodium series of stripped atoms is exhibited in Fig. 14.5.

(2) On the other hand, if we compare two levels in the same atomic system, having the same value of l, and consequently the same value of σ_1, but with the values $j_1 = l + \frac{1}{2}$, and $j_2 = l - \frac{1}{2}$, the energy values of the levels are given by

$$W_{n,l,j} = \frac{Rch(Z - \sigma_1)^2}{n^2} + \frac{\alpha^2 Rch(Z - \sigma_2)^4}{n^3}\left\{\frac{1}{j + \frac{1}{2}} - \frac{3}{4n}\right\}, \tag{14.17}$$

where j denotes either j_1 or j_2.

For $j_1 = l + \frac{1}{2}$, this relation becomes

$$W_{n,l,j} = \frac{Rch(Z - \sigma_1)^2}{n^2} + \frac{\alpha^2 Rch(Z - \sigma_2)^4}{n^3}\left(\frac{1}{l + 1} - \frac{3}{4n}\right), \tag{14.18}$$

which is identical with Sommerfeld's relation, equation (14.7), derived on the basis of the theory of relativity alone, with $k = l + 1$.

For the difference in energy between two doublet levels having the inner quantum numbers, $j_1 = l + \frac{1}{2}$ and $j_2 = l - \frac{1}{2}$, it readily follows that

$$E_{n,l,j_2} - E_{n,l,j_1} = \frac{\alpha^2 Rch(Z - \sigma_2)^4}{n^3 l(l + 1)}, \tag{14.19}$$

which is identical with equations (14.8) and (14.12), since $l = 1$ is the lowest value of l for which two different values of j can occur. Hence (14.19) expresses the law for *regular doublets*, and as shown already, this relation may be used to calculate the value of the screening constant.

Because the difference in energy arises from the difference in electron spin these doublets are customarily designated now as *spin doublets*.

From these deductions it follows as stated previously, that the L_I level must be of the same type as $S_{1/2}$, while L_{II} and L_{III} must be analogous to $P_{1/2}$ and $P_{3/2}$ respectively, as shown in Table 14.2. Thus the same explanation is

cm^{-1}

$\nu = 3^2\,S_{\frac{1}{2}} - 3^2\,P_{\frac{1}{2}}$

| | 11 | 12 | 13 | 14 | 15 | 16 | 17 |
| | Na I | Mg II | Al III | Si IV | P V | S VI | Cl VII |
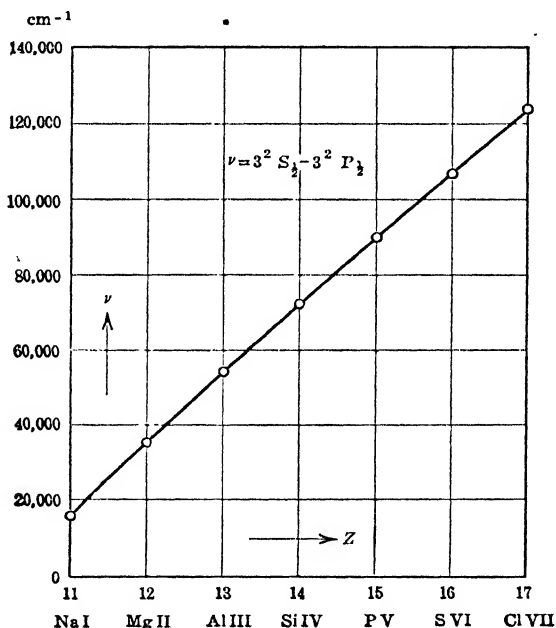
Fig. 14.5. First Members of Principal Series for Sodium-Like Atoms, Illustrating Irregular Doublet Law. (In this plot ν = wave number)

found to apply to the two types of doublets in optical and X-ray spectra. The resemblance is accounted for by the fact that while doublets in optical spectra are due to the presence of a single valence-electron outside a completed "shell," X-ray spectra are due to the removal of a single electron from a completed shell nearer to the nucleus. According to the Pauli-Hund theory, the type of spectral terms should be the same in both cases, as will be pointed out in a subsequent section.

Similarly by removal of two electrons from an inner shell, X-ray terms are obtained which resemble those of the Ca-group. G. Wentzel [1] has designated

[1] *Z. Physik*, **31**, 441 (1925).

these as *X-ray spark spectra*. Further details with regard to spectra of this nature have also been published by L. A. Turner.[1]
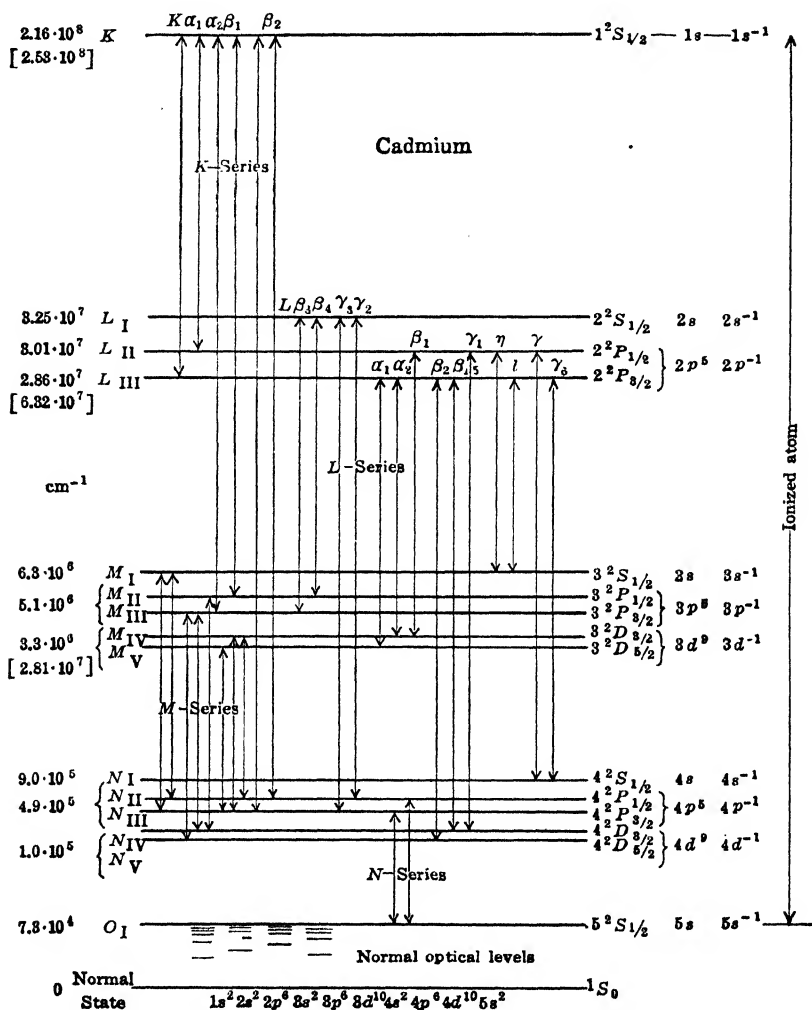
FIG. 14.6. Complete Energy Level Diagram for Cadmium Illustrating Relation Between Optical and X-Ray Levels

It should be added here that the relations for the spin and irregular doublet levels as given in the above series of equations represent a first approximation, valid only for lower values of $Z - \sigma$. The complete equations contain terms

[1] *Phys. Rev.*, **26**, 143 (1925).

involving $\alpha^4(Z - \sigma_3)^6/n^6$, $\alpha^6(Z - \sigma_4)^8/n^8$, etc., which become of increasing importance with increase in Z. That the screening constant is not necessarily the same for all these terms is indicated by the values σ_3, σ_4, etc. Thus the more rigorous expression for the separation in wave numbers for the L_{II}-L_{III} doublet is given by the equation

$$\Delta\bar{\nu} = \frac{R\alpha^2(Z - \sigma_2)^4}{2^4}\left\{ 1 + \frac{5\alpha^2}{2^3}(Z - \sigma_2)^2 + \frac{5\alpha^4}{2^7}(Z - \sigma_2)^4 + \cdots \right\}.$$

As illustrating the relative energies of the X-ray and optical levels, Fig. 14.6 shows a complete energy level diagram for cadmium.[1]

The electron configuration for the normal state and corresponding spectral term are shown at the bottom. Removal of one of the $5s$ electrons (indicated by $5s^{-1}$ at the lower right-hand side) requires an energy corresponding to the wave number 7.3×10^4, i.e., 8.99 electron volts. This is the ionization potential for the atom, as shown in Table 13.2. All the optical levels fall in this range of energy values.

By removal of "inner" electrons of type $4d$, $4s$, etc., the different X-ray levels are obtained. Thus the removal of one of the $2s$ electrons raises the atom to state L_I, and finally the removal of one of the $1s$ electrons raises the atom to state K. "The term values given at the left in the figure show that the binding energy of a $1s$ electron is about 3000 times that of a $5s$ valence electron."

15. MULTIPLET LEVELS IN OPTICAL SPECTRA

(1) **Hydrogen Fine Structure:** In the previous section reference was made to Sommerfeld's interpretation of the fine structure observed for spectral lines in hydrogen. When the H_α and H_β lines of the Balmer series are investigated under conditions of high resolution, it is observed that these lines are actually doublets, with a wave number separation between components of 0.365 cm.$^{-1}$. While Sommerfeld interpreted this as due to the relativity effect, it was shown by Heisenberg and Jordan that the separation is actually due to a combination of the relativity effect and spin-orbit interaction. Furthermore the latter showed that by proper assignment of values of l and j to the spectral terms the analogy could be demonstrated between the spectral terms for hydrogen and those for the alkali elements, as would be expected from the fact that in both cases the terms are due to a single valence electron.

Figure 15.1 shows the energy levels (excluding that corresponding to $n = 1$) and transitions on the basis of the present views.

The Sommerfeld notation of n and k values for the levels is given on the left-hand side, while the values of l and j which must be assigned to these levels on the basis of the Heisenberg-Jordan relation are given on the right-hand side. The S and $P_{1/2}$ levels, $P_{3/2}$ and $D_{3/2}$ levels are shown slightly separated, although

[1] Fig. 16.11, H. E. W., *op. cit.*, p. 310.

they *actually coincide*, since the effective nuclear charge is the same, i.e., unity, in all cases. That is, the *irregular doublet separation is not present*, and consequently each group of transitions which is indicated by a bracket located across
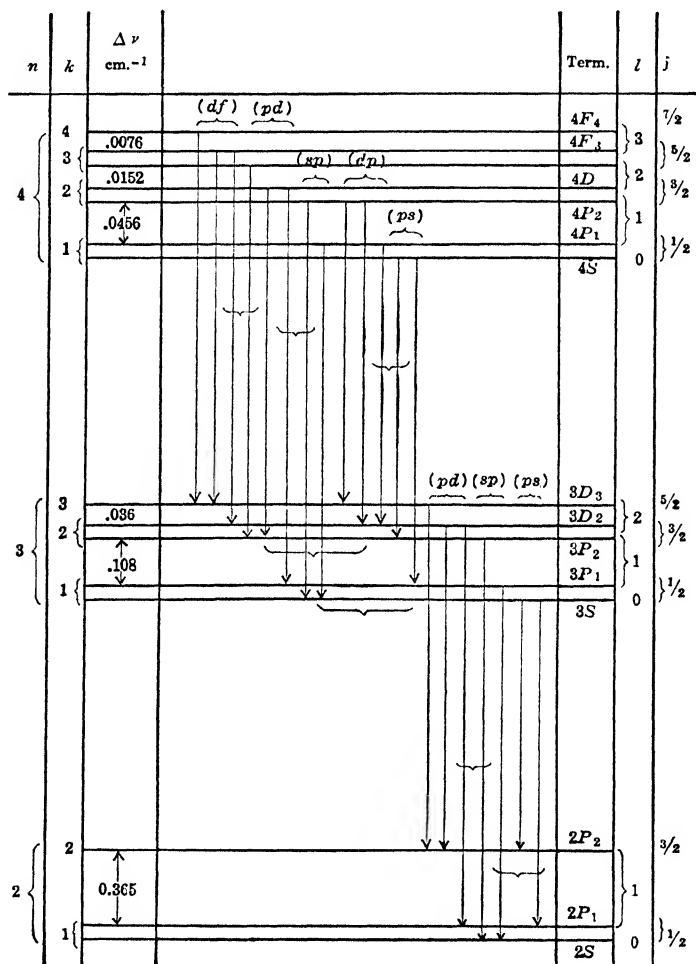

Fig. 15.1. Energy Levels of Hydrogen Atom as Related to Energy Levels of Alkali Atoms, According to Unsöld. (Following the practice at that time the subscript corresponded to the value $j + \frac{1}{2}$ for doublet levels)

the vertical lines refers to the same spectral line. The corresponding transitions in spectra of the alkali metals are indicated by the notation (pd), (sp), (df), etc., while the values of $\Delta\tilde{\nu}$ calculated by equation (14.17) are indicated for the different doublet levels.

The diagram thus exhibits the resemblance between the spectrum of hydrogen and the spectra of other atoms with a single valence electron on the one hand, and X-ray spectra on the other.

(2) **Energy Levels for Helium:** Fig. 15.2 [1] shows the energy levels observed in the spectrum of helium. These levels can be arranged in two systems, and it was assumed for a long time that ordinary helium consists of two elements, designated as *orthohelium* and *parhelium*. The former is characterized by a spectrum of what was at one time regarded as a system of doublet terms, but
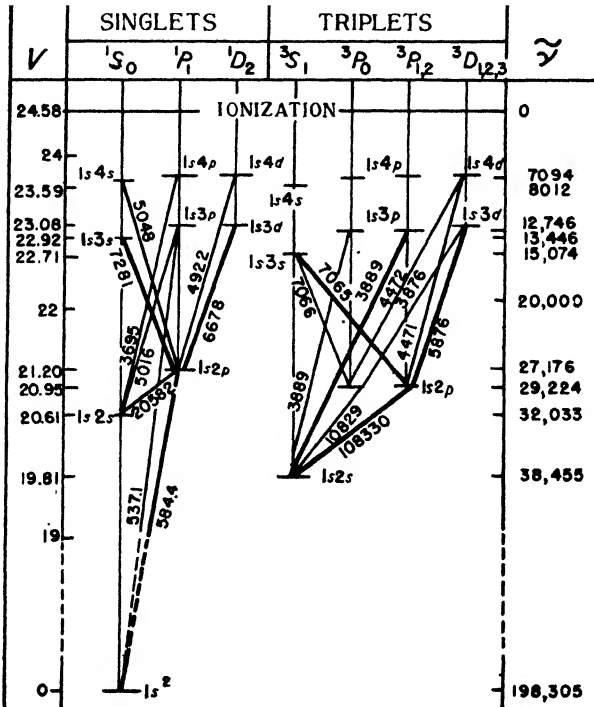
Fig. 15.2. Energy Level Diagram for Helium

which is now known to be in reality a *triplet* system (as would be expected by analogy with other atoms which have two valence electrons in s-states, such as Ca and Hg). On the other hand, the parhelium spectrum consists of *singlet* terms. The energy level diagram shown in Fig. 15.2 is based on the measurements of critical potentials by Franck and Knipping [2] and on the investigations by Hertz [3] and Lyman,[4] of the extreme ultra-violet spectrum of the gas.

[1] Fig. 53, Ref. S. D. (revised).

[2] *Physik. Z.*, **20**, 418 (1919); *Z. Physik*, **1**, 320 (1920).

[3] *Ibid.*, **22**, 13 (1924).

[4] *Astrophys. J.*, **60**, 1 (1924).

Each level is designated by the quantum states of the two electrons, and it will be observed that there are two levels of type 1s2s, and three of type 1s2p.* Furthermore there are no transitions from the 1s2s levels to the ground state. These are known as *metastable states* and will be discussed in a subsequent section.

On the basis of the Bohr theory, with its concept of 1s electrons revolving in circular orbits, it was assumed that in the normal (1s²) state the two electrons revolve in very slightly elliptical orbits inclined at an angle of 120° to each other, as shown in Fig. 15.3,—hence the designation "crossed-orbit" model. However, all attempts by the foremost theoretical physicists to derive the ionization energy of such a system on the basis of classical mechanics proved unsuccessful, and it was only by the application of the methods of wave mechanics that a satisfactory solution of the problem was obtained, including an explanation of the observed occurrence of two systems of energy levels. While the more detailed mathematical procedure involved in this solution is given in different treatises on quantum mechanics, it is of interest to present here a brief summary of the method used and of the significant results deduced.

Fɪɢ. 15.3.   Crossed Orbit Model of Helium Atom

For the system consisting of a nucleus of charge Ze and two electrons (designated 1 and 2), the Schroedinger differential equation assumes the form,

$$\nabla_1^2\phi + \nabla_2^2\phi + \frac{8\pi^2 m}{h^2}\left(E + \frac{Ze^2}{r_1} + \frac{Ze^2}{r_2} - \frac{e^2}{r_{12}}\right)\phi = 0, \qquad (15.1)$$

where r_1 and r_2 are the distances of the electrons from the nucleus and r_{12} denotes the interelectronic distance, while ∇_1^2 and ∇_2^2 represent the Laplacian operators with respect to the coordinates of each electron.

Let us consider first the normal state, in which the two electrons are in 1s states and must therefore possess opposite spins.   The first two terms involving the Laplacians represent the kinetic energy of the electrons, the last three terms in the bracket represent the potential energy of the electrons.   In solving equation (15.1) a well-known principle is applied, viz: the correct solution will be that for which E, the total energy, that is the sum of kinetic and potential energy, is a minimum.   The procedure used consists in substituting for ϕ some plausible function and determining the values of certain arbitrary parameters which will make E a minimum.   This is known as the *variational method* and

---

* Two of these (in the column $^3P_{2, 1}$) are so close together that the separation cannot be indicated in the diagram.

has proved extremely useful in solving many problems in physics. By means of this method it has been found possible to deduce a value for the ionization potential of helium which is in very good agreement with the spectroscopically observed value (from the wave number of the normal term).

In the excited state of the helium atom, one of the electrons is in a state of quantum numbers n, l, m, with which is associated an eigenfunction which we shall designate by $\phi_n(r_2)$ and the other in the $1s$ state, which is represented by the eigenfunction $\phi_1(r_1)$.

If it were not for the presence of the term e^2/r_{12} which represents the repulsive energy between the electrons, the solution of equation (15.1) would be the same as for two independent hydrogen-like atoms. That is, the eigenfunction would be represented by

$$\phi_{1n} = \phi_1(r_1)\phi_n(r_2), \tag{15.2}$$

where ϕ_1 and ϕ_n are the eigenfunctions for electrons in hydrogen-like atoms, and the energy states would be given by

$$E_0 = E_1 + E_n$$
$$= -Rch\left(\frac{Z^2}{1^2} + \frac{Z^2}{n^2}\right). \tag{15.3}$$

But the *same* value of the energy would be obtained if the electrons were interchanged with respect to quantum states. In that case the eigenfunction for the system would have the form

$$\phi_{n1} = \phi_n(r_1)\phi_1(r_2). \tag{15.4}$$

Both eigenfunctions, ϕ_{1n} and ϕ_{n1}, represent the same energy state and we therefore have here a case of *two-fold degeneracy*, which arises from the *possibility of interchanging the two electrons*. An analogous condition occurs when two identical pendulums or oscillating systems of identical frequency, ν, are coupled together. Owing to interaction, the system as a whole exhibits two new frequencies, $\nu_1 = \nu - \Delta\nu$, and $\nu_2 = \nu + \Delta\nu$, where $\Delta\nu$ is, in general, small compared to ν.

These two frequencies correspond to the two so-called *normal modes* of vibration of a system of coupled *identical* oscillators, which are illustrated in Fig. 15.4. In one of them, ν_1, which is less than ν, the pendulums (which may be regarded as typical oscil-

Fig. 15.4. Illustrating the Two Modes of Vibration of Two Interacting Pendulums

lators) *vibrate in phase*, and in the other, ν_2, with *opposite phase*. Hence, these are designated as the *symmetric* and *antisymmetric* modes, respectively. The actual motion of the pendulums is the result of a superposition of the two

modes, as shown in Fig. 15.5. The following description of the behavior of the system is taken from the discussion of this topic by N. F. Mott.[1]
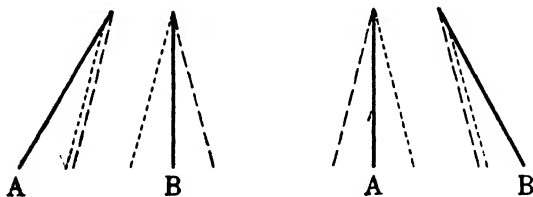

FIG. 15.5.   Motion of Each Pendulum as a Superposition of the Two Modes

"One can see that ν_2 is greater than ν, and ν_1 less than ν. For when they are swinging in opposite phase, the pendulums are, so to speak, pulling one another back all the time, and so increasing the restoring couple. The frequency must therefore be greater than it would be in the absence of one of the pendulums. When the pendulums are swinging in the same phase, the opposite is the case; the pendulums help each other to swing outwards, the restoring couple is decreased, and so the frequency is less than it would otherwise be. One can also see that the amount by which ν_1 and ν_2 differ from ν depends on the strength of the coupling between the pendulums. For instance, if the string on which the pendulums are hung be fairly tight, and the two pendulums are hung very near to opposite ends of the string, then ν_1 and ν_2 will not differ from ν by as much as they would if the pendulums were hung nearer to the middle of the string. It is on the existence of these two different frequencies ν_1 and ν_2 that the slow exchange of energy from one pendulum to the other and back depends."

An analogous phenomenon occurs in the helium atom since the system can pass from the state described by the eigenfunction ϕ_{1n} to that described by ϕ_{n1}, and it is concluded from this that the actual state of the system should be represented, to a first order approximation, by the two eigenfunctions
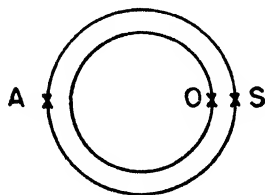
FIG. 15.6.   Symmetric and Antisymmetric States of Excited Helium Atom

$$
\left.
\begin{aligned}
F_S &= \phi_{1n} + \phi_{n1} \\
F_A &= \phi_{1n} - \phi_{n1}
\end{aligned}
\right\}, \qquad (15.5)
$$

in one of which, F_S, the two electrons are in the *symmetric* mode, and in the other, F_A, in the *antisymmetric mode*. The difference between these two states may be represented diagrammatically by Fig. 15.6 which is taken from the discussion of this topic by C. G. Darwin.[2]

The two circles represent two Bohr orbits with angular momenta differing by one quantum ($n_1 = 1$, $n_2 = 2$). As Darwin points out, "If one electron is found to be at O, then in the symmetric mode the other is most likely to be at S, whereas in the antisymmetric mode it is most likely to be at A."

[1] An Outline of Wave Mechanics, Cambridge University Press, Cambridge, 1930 (Chapter VI).

[2] The New Conception of Matter, The Macmillan Company, New York, 1931, p. 205. See also discussion by S. D., *op. cit.*, p. 274, et seq.

The function F_S is of the type known as *symmetrical* because an interchange of the coordinates of the two electrons leaves the sign of the function unaltered. On the other hand, the function F_A is of the *antisymmetrical* type, because it does change sign when the coordinates are interchanged.

From this point of view it follows that the energy E_S, corresponding to F_S, must be less, numerically, than E_A, which corresponds to F_A. For in the antisymmetric state the repulsive energy between the two electrons must be less than in the symmetric case, and consequently the net attractive energy between each electron and the nucleus will be greater.

Actually it is found, by solving the Schroedinger equation, that the so-called zeroth order eigenvalues for the excited states of the helium atom are represented by

and

$$\left. \begin{array}{l} E_S = E_0 + \eta_c + \eta_e \\ \\ E_A = E_0 + \eta_c - \eta_e \end{array} \right\}, \tag{15.6}$$

where E_0 has been defined already in equation (15.3), η_c represents the resultant energy due to repulsion between the electrons and attraction between each electron and the nucleus, (and is therefore known as the *coulomb energy*), while η_e represents a non-classical term, known as the *resonance* or *exchange* energy. The latter arises, as stated above, from the fact that the two electrons can interchange orbits, and η_e/h represents the frequency of this interchange.

For the state $n_1 = 1$, $n_2 = 2$, the values obtained for the two eigenvalues are

$$\left. \begin{array}{l} \dfrac{E_S}{Rch} = -(1 + \frac{1}{4})Z^2 + 0.420Z + 0.044Z \\ \\ \dfrac{E_A}{Rch} = -(1 + \frac{1}{4})Z^2 + 0.420Z - 0.044Z \end{array} \right\}, \tag{15.7}$$

where Z represents the charge on the nucleus ($Z = 2$ for He). Thus E_S and E_A represent energy levels which are located symmetrically about the energy level $E/Rch = -(1 + \frac{1}{4})Z^2 + 0.420Z$, and the level corresponding to E_A is *lower*, that is, represents a greater binding energy for the two electrons.

For any given value of n, E_A is lower than E_S. Now it will be observed that the $1s2s$ level in orthohelium is lower than the $1s2s$ level in parhelium, and a similar relation exists between the $1s2p$ levels in both systems. Consequently the *parhelium terms must correspond to the symmetrical eigenfunctions*, and the *orthohelium terms to the antisymmetrical eigenfunctions*.

While we thus derive an explanation for the occurrence of the two systems of series for helium, it does not afford an explanation for the existence of triplets and singlets. This may be obtained by introducing both electron spin and a criterion first enunciated by Pauli.

As pointed out previously, the Pauli principle leads to the conclusion that in the normal state of the helium atom, the two electrons must have opposite spins. Now it is assumed that corresponding to this spin there exists an

eigenfunction $\psi(s)$, which designates the orientation of the axis of spin in a magnetic field. Designating the functions for the two electrons by $\psi(s_1)$ and $\psi(s_2)$, the *complete spin function* may be represented by any one of the four combinations shown in the last column of the following table. The first two columns give the corresponding values of m_s and the third that of $M = m_{s_1} + m_{s_2}$.

m_{s_1}	m_{s_2}	M	Eigenfunction
$\frac{1}{2}$	$\frac{1}{2}$	1	$\psi(\frac{1}{2})\psi(\frac{1}{2}) = \alpha$
$\frac{1}{2}$	$-\frac{1}{2}$	0	$\psi(\frac{1}{2})\psi(-\frac{1}{2}) = \beta$
$-\frac{1}{2}$	$\frac{1}{2}$	0	$\psi(-\frac{1}{2})\psi(\frac{1}{2}) = \gamma$
$-\frac{1}{2}$	$-\frac{1}{2}$	-1	$\psi(-\frac{1}{2})\psi(-\frac{1}{2}) = \delta$

The eigenfunctions β and γ correspond to the same value of M, and thus represent a degenerate state. For the perturbed state (that is for the state in which the electrons interact) these eigenfunctions must be replaced by $\beta + \gamma$ and $\beta - \gamma$.[1] We thus obtain three functions which are symmetrical in the electron spins, viz:

$$\alpha, \beta + \gamma, \text{ and } \delta$$

and one which is antisymmetrical, viz., $\beta - \gamma$. The first set gives rise to triplet terms for which the values of M are 1, 0, and -1, and the last function corresponds to the singlet term, $M = 0$.

The complete eigenfunction for any state of the system is the product of the *orbital and spin functions*. Now Pauli's principle states that the complete eigenfunction for an atomic system must be of the *antisymmetrical type*. We thus obtain the following four functions to represent an excited state of the helium atom:

$$F_S(\beta - \gamma); \quad F_A\alpha, \quad F_A(\beta + \gamma), \quad F_A\delta.$$

Since the spins in parhelium are opposed, the first function must represent this series, and the remaining three, the orthohelium series, which is in agreement with the observed occurrence of triplets in this system.

Furthermore it has been shown that in absence of any spin-orbit interaction no transition can occur between a state of type F_S and one of type F_A.

While Lyman[2] had observed in the spectrum of helium, a line $\lambda 591.6$ which was interpreted as the intercombination line $1^1S_0 - {}^3P_1$, it was shown subsequently by H. D. Dorgelo[3] that this line must actually have been due to a trace of neon in the helium.

However, in the case of more complex atoms, the spin-orbit interaction is so strong that many intercombination lines are obtained. For instance, the

---

[1] In this case, as well as in equation (15.5), a factor $1/\sqrt{2}$ has been omitted, in order to simplify the argument. See ref. S. D., pp. 280–1.

[2] Lyman, *Astrophys. J.*, 60, 1 (1924).

[3] *Physica*, 6, 150 (1926).

Hg line λ2537 which corresponds to the transition $^1S_0 - {}^3P_1$ is very intense, especially in a discharge in a low pressure of mercury vapor.

(3) **Two-electron Transitions:** In accounting for the origin of lines in the spectra of hydrogen, ionized helium and of the alkali elements, it has been assumed that these lines are due to transitions of a single electron between two different electronic states. This view is however not adequate to account for higher multiplet levels and the observations on the resulting transitions.

Although Heisenberg, Landé and others had formally derived certain rules by which they could calculate the nature of the multiplet levels formed by successive addition of electrons, there existed certain theoretical difficulties in the whole scheme. While the conception of the spinning electron served to remove some of these difficulties, the evidence brought forward by Russell and Saunders for the simultaneous transition of two electrons helped materially in clarifying the whole problem of complex spectra.

It was known for some time that in the spectrum of Ca there exist not only the two systems of singlet and triplet terms mentioned already, but also a so-called *anomalous* * group of terms for which the limiting terms (corresponding to the ionizing potential in the normal spectra of the alkali and alkaline earth metals) have *negative* values.
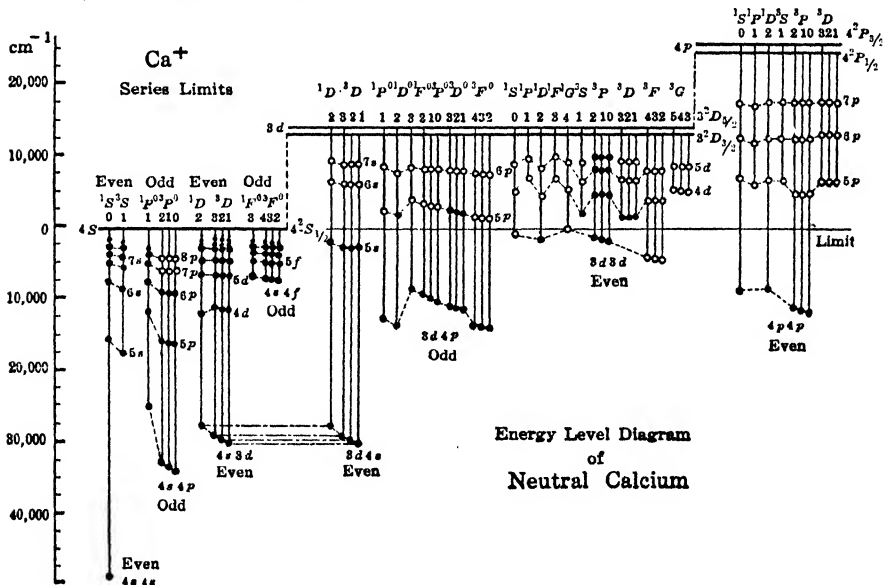
Fig. 15.7. Complete Energy Level Diagram for Ca, Showing *Negative* Terms

Figure 15.7 [1] which gives a more complete energy level diagram for calcium shows the presence of two such sets of levels (marked 3d and 4p) which are

---

* These are also known as "displaced" terms.
[1] Ref., H. E. W., p. 182.

located above the limit (indicated by wave number 0) for the normal terms in the spectrum.   This limit corresponds to the removal of one of the $4s$ electrons, leaving Ca^+ (for which the ionization energy derived from the wave number of the normal $^1S_0$ level, $\bar{\nu} = 49305$, is 6.11 volts).

As an explanation for the occurrence of terms for which the limit is 13961 cm.$^{-1}$ (that is, 1.73 volts) above the ionization potential, Russell and Saunders suggested that these terms correspond to a set of energy states in which one of the valence electrons is in a $3d$ state, while the other occupies successively the states $3d$, $4d$, etc., or $4p$, $5p$, etc.

This suggestion was in agreement with the observation that in the spectrum of Ca^+, which is a doublet system, like that of K, the first excited state, which corresponds to excitation of the single valence electron to a $3d$ state, lies 1.70 volts above the ground level.

That the electron configuration $4s3d$ has a higher energy value than $4s^2$ is evidenced by the fact that in building up electron configurations, the two $4s$ levels are filled first (see Table 13.2) and then the $3d$ level, as shown by the spectra of K ($Z = 19$), Ca ($Z = 20$) and Sc ($Z = 21$).

Furthermore, since the excitation of the $4s$ electron in Ca^+ to a $4p$ level requires 3.1 volts (which agrees well with the observed limit at about 25,000 cm.$^{-1}$ above the ionization potential for Ca), this latter level could be accounted for by assuming that one of the valence electrons in Ca is excited to the $4p$ state, while the other electron occupies successively the states $4p$, $5p$, etc.

Thus the negative terms must be due to the occurrence of *simultaneous transitions* of one of the two valence electrons from the $4s$ to a $3d$ or $4p$ level, and of the other electron from the $4s$ to some other level.   When *both electrons* return to lower levels a *monochromatic radiation* is emitted, just as in the case of a single electron.

From an analysis of the transitions between terms in these anomalous terms and the normal terms (those having as a limit the ground term $4^2S_{1/2}$ of Ca^+) it was found possible on the basis of the selection rules to assign to the former values of L, S and J.   In this manner it was observed, for instance, that transitions occur between $^3P'$ terms in the anomalous series and normal ^3P terms, and also between $^3D'$ terms in the former and normal ^3D terms, the primes being used to indicate the observation that these terms could combine with other terms having the *same value of L*.   Also, double primes were introduced to indicate terms in the anomalous series which do not combine with normal terms in accordance with the selection rule, $\Delta L = \pm 1$.

Russell and Saunders showed that their deductions regarding the spectral symbols to be assigned to these anomalous, as well as to normal, terms could be accounted for on the following basis, which forms an extension of the vector-model used in interpreting the relations between l, s and j for terms in the spectra of the alkalis.[1]

It is assumed that interaction between the s-vectors of two electrons is stronger than that between the s-vector of any one electron and its l-vector,

[1] See Section 11(3).

and similarly for the *l*-vectors. As a consequence, the *l*-vectors of the two electrons interact to form a resultant *L*-vector; similarly the *s*-vectors combine to form an *S*-vector, and the resultant of *L* and *S* gives rise to a *J*-vector for the *particular term*. As an illustration of the application of this procedure, let us consider the nature of the terms which can result from the interaction of a $4s(l_1 = 0)$ and $3d(l_2 = 2)$ electron. The resultant *L*-vector can have only the single value $L = 2 + 0 = 2$. Since $s_1 = \pm\ s_2 = \pm\ \frac{1}{2}$, the resultant values of *S* are 0 or 1, corresponding to singlet and triplet terms respectively. Furthermore, since the possible values of *J* are $J = 2 + 1, 2 + 0, 2 - 1 = 3, 2, 1$, it follows that the resulting spectral terms should be of type $^1D_2$ and $^3D_{1,2,3}$.

In a similar manner the nature of the spectral term may be derived, as will be described more fully in the following section, for the interaction of two electrons in any other types of spectral states.

As mentioned above it has been observed that transitions between anomalous and normal terms occur for which $\Delta L = 0$, thus apparently violating the selection rule enunciated previously, viz., $\Delta L = \pm 1$. This was the reason for adopting symbols such as $^1D_2'$ and $^3P'_{0,1,2}$ to differentiate anomalous terms from normal terms, having the same value of *L*, with which they combine.

However, Heisenberg showed, on the basis of theoretical considerations, that in those cases where two electrons jump simultaneously, $\Delta l_1 = \pm 1$, and $\Delta l_2 = 0$ or ± 2. This conclusion, which has been verified by observation is illustrated by the following transitions, which are observed in the spectrum of calcium:

(1) $^3P' \rightarrow\ ^3P$, that is, $3d6d(^3P)$, with $l_1 + l_2 = 4$, to $4s4p(^3P^0)$ with $l_1 + l_2 = 1$. Thus, $\Delta l_1 = -2, \Delta l_2 = 1$.

(2) $^3P'' \rightarrow\ ^1D$, that is, $3d4p(^3P^0)$ with $l_1 + l_2 = 3$, to $3d4s(^1D)$, with $l_1 + l_2 = 2$. Thus $\Delta l_1 = 0, \Delta l_2 = -1$.

(3) $^3F'' \rightarrow\ ^1D$, that is, $3d4p(^3F^0)$, with $l_1 + l_2 = 3$, to $4s3d(^1D)$, with $l_1 + l_2 = 2$. Thus $\Delta l_1 = -2, \Delta l_2 = +1$.

(4) $^3D' \rightarrow\ ^1S$, that is, $3d4p(^3D^0)$ with $l_1 + l_2 = 3$, to $4s4s(^1S_0)$, with $l_1 + l_2 = 0$. Thus $\Delta l_1 = -2, \Delta l_2 = -1$.

These transitions also illustrate an empirical rule deduced by O. Laporte, according to which transitions are permitted only from a state for which Σl_i is odd to one for which it is even, or vice versa. Consequently it is customary to classify terms into two groups, *odd* and *even*. Formerly the odd terms were indicated by a prime at the upper right-hand corner of the spectral symbol, thus $^3P'$, $^2D'$, and so forth. More recently a small superscript ^{0} is used instead. For instance, the possible spectral terms for the configuration $3d \cdot mp$ ($\Sigma l = 3$) are $^1P_1^0$, $^1D_2^0$, $^1F_3^0$, $^3P^0_{0,1,2}$, $^3D^0_{1,2,3}$ and $^3F^0_{2,3,4}$. As will be pointed out in a subsequent section the distinction between odd and even terms has a quantum mechanical basis.

Finally it should be mentioned that anomalous (or displaced) terms have been observed in the spectra of other elements of the second group and in

spectra of atoms of greater complexity in both the normal and partially stripped states.

(4) **Derivation of Terms in Complex Spectra:** The observations on the occurrence of negative terms led Russell and Saunders to formulate a method of deriving terms in complex spectra which has been described briefly in a previous section and is known as the *LS*-coupling method. As pointed out already, it is extremely difficult to solve the Schroedinger equation for a system of many electrons without introducing certain assumptions regarding the probable form of the orbital functions. The Russell-Saunders method represents one such procedure for overcoming the mathematical difficulties, and another method will be described below.

In this connection it is desirable to review briefly the remarks on spectral notation which have been made in previous sections.[1]

The state of a *single* electron is ordinarily designated by *four* quantum numbers: (*a*) n, the principal or total number, which determines to a first approximation the energy of the state; (*b*) l, the "serial" quantum number, which serves to designate the type of orbital (s, p, d, f, etc.); (*c*) m_l, the magnetic quantum number which designates the orientation of the orbit in a magnetic field; (*d*) m_s, the magnetic quantum number which designates the direction of electron spin in a magnetic field.

The quantum numbers m_l and m_s indicate that the projections of the angular momentum vectors l and s in the direction of a magnetic field are quantized in space, that is, *only certain orientations of the orbit and of the direction of spin are possible.*

It is to be observed, furthermore, that

$$l = n - 1, n - 2, \cdots 0,$$
$$m_l = l, l - 1, \cdots - (l - 1), - l,$$
$$m_s = \pm \tfrac{1}{2}.$$

Thus there are but two possible directions of spin of the electron, 180° apart.

The *state of an atomic system* is defined by three numbers: (*a*) the "serial" quantum number, L, which is the resultant of the l-vectors for the individual electrons, and which designates the type of system according to the following table:

L:	0	1	2	3	4	5	6	7
Type:	*S*	*P*	*D*	*F*	*H*	*K*	*L*	

(*b*) the spin quantum number S which corresponds to the resultant of the spin vectors of the individual electrons, and (*c*) the inner quantum number, J, which

---

[1] Notable contributions on the derivation of terms in complex spectra and on the notation of spectral terms were made not only by Russell and Saunders but also F. Hund, who has discussed this topic very comprehensively in his book, Linienspektren und periodisches System der Elemente, Julius Springer, Berlin (1927). See also refs. P. G., H. E. W. and G. H.

represents the total number of units of angular momentum of the atomic system for the given state, and which is the resultant (vectorially) of L and S.

The value of S determines the multiplicity, r, of the system which is given by the relation

$$r = 2S + 1. \tag{15.8}$$

Hence $r = 1$ (singlets) for $S = 0$; $r = 2$ (doublets) for $S = \frac{1}{2}$, and so forth. As mentioned previously, the multiplicity is indicated by an index at the upper left-hand corner of the symbol for the series; while the value of J is shown by an index at the lower right-hand corner.

The method which has just been described for determining the nature of a spectral term is that of Russell and Saunders and may be represented symbolically by the relations

$$(s_1 s_2 \cdots)(l_1 l_2 \cdots) = (S, L) = J, \tag{15.9}$$

$$J = L + S, L + S - 1, \cdots, |L - S|. \tag{15.10}$$

As an application of this method let us consider the nature of the terms resulting from the interaction of two electrons of spectral types $n_1 p$ and $n_2 d$. Since the actual values of n_1 and n_2 are immaterial in this connection we may omit any consideration of these numbers and merely inquire into the result of the interaction of a p-electron ($l_1 = 1$) and a d-electron ($l_2 = 2$). The resultant values of S are $S = 0$ for antiparallel spins and $S = 1$ for parallel spins. These values of S correspond to singlet and triplet terms respectively. The resultant values of L are $L = 3$, 2 and 1, corresponding to F, D and P terms respectively. Coupling the values of S with those of L we obtain the following terms:

$J = 3, 2, 1$, corresponding to $L = 3$, $L = 2$, $L = 1$, $S = 0$,
$J = 4, 3, 2$, corresponding to $L = 3$, $S = 1$,
$J = 3, 2, 1$, corresponding to $L = 2$, $S = 1$,
$J = 2, 1, 0$, corresponding to $L = 1$, $S = 1$.

The first set of three terms have the spectral symbols $^1F_3$, $^1D_2$ and $^1P_1$. The second set have the symbols $^3F_4$, $^3F_3$ and $^3F_2$, the third set, $^3D_3$, $^3D_2$ and $^3D_1$, and the last set, $^3P_2$, $^3P_1$ and $^3P_0$.

As another illustration let us consider the interaction of s and p electrons, on the one hand, and s and d electrons on the other, such as are observed in the spectrum of helium. In the first case, $l_1 = 1$, $l_2 = 0$, hence $L = 1$, $S = 0$ or 1, and $J = 2, 1, 0$, and 1. The resulting terms are therefore $^3P_2$, $^3P_1$, $^3P_0$ and $^1P_1$.

For the second case, $l_1 = 2$, $l_2 = 0$. Hence $L = 2$, $S = 0$ or 1, and $J = 3, 2, 1$, and 2. The resulting terms are therefore, $^3D_3$, $^3D_2$, $^3D_1$ and $^1D_2$. Both these sets of terms are shown in the energy level diagram for helium, Fig. 15.2.

The method used above is applicable to the interaction of *non-equivalent* electrons, that is, electrons belonging to different orbital types (different values of n and different values of l). In the case, however, of *equivalent* electrons, that is, electrons for which $n_1 = n_2$ and $l_1 = l_2$ we must take into account the Pauli exclusion principle, which states that for two such electrons the values of m_s must be $+\frac{1}{2}$ and $-\frac{1}{2}$ respectively. This excludes certain terms which would occur in the interaction of non-equivalent electrons.

The procedure used in deriving the spectral terms for equivalent electrons is that developed by F. Hund and may be illustrated by its application to the interaction of two electrons of type $3d$.

TABLE 15.1

$n_2 = n_1 = 3;\quad l_1 = l_2 = 2$

m_{l_1}	m_{l_2}	m_{s_1}	m_{s_2}	M_L	M_S	M
2	2	$+\frac{1}{2}$	$-\frac{1}{2}$	4	0	4
	1	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	3	100-1	4332
	0	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	2	100-1	3221
	-1	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	1	100-1	2110
	-2	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	0	100-1	100-1
1	1	$+\frac{1}{2}$	$-\frac{1}{2}$	2	0	2
	0	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	1	100-1	2110
	-1	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	0	100-1	100-1
	-2	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	-1	100-1	0-1-1-2
0	0	$+\frac{1}{2}$	$-\frac{1}{2}$	0	0	0
0	-1	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	-1	100-1	0-1-1-2
0	-2	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	-2	100-1	-1-2-2-3
-1	-1	$+\frac{1}{2}$	$-\frac{1}{2}$	-2	0	-2
-1	-2	$\pm\frac{1}{2}$	$\pm\frac{1}{2}$	-3	100-1	-2-3-3-4
-2	-2	$+\frac{1}{2}$	$-\frac{1}{2}$	-4	0	-4

Table 15.1 shows the procedure in detail. Adding the values of m_l for each electron and those of m_s we obtain the values tabulated under M_L and M_S respectively. These, in turn, when added yield the values of $M = M_L + M_S$ given in the last column. It will be observed that for values of $m_{l_1} = m_{l_2}$, only two values of m_s are possible, so that $M_S = 0$. For $m_{l_1} \neq m_{l_2}$, four values of M_S are obtained, viz., 1, 0, 0 and -1. This shows that the terms will be either singlets or triplets. Also, since

$$M = J, J - 1, \cdots, - J$$

it is possible by arranging the values of M as in Table 15.2 to deduce the corresponding values of J. Furthermore, since L can have the values 4, 3, 2, 1, 0 it follows that the terms will be of types G, F, D, P and S, and that the values of J will be distributed among these types. These considerations lead to the conclusion that the only possible spectral types of terms are those indicated in the last column in Table 15.2.

TABLE 15.2

Values of M (Table 15.1)									Corresponding Value of J	Spectral Term
4	3	2	1	0	-1	-2	-3	-4....	4	$^1G_4$
4	3	2	1	0	-1	-2	-3	-4..	4	$^3F_4$
		2	1	0	-1	-2	-3	... .	3	$^3F_3$
		2	1	0	-1	-2		....	2	$^3F_2$
		2	1	0	-1	-2		. . ..	2	$^1D_2$
		2	1	0	-1	-2		.. ... .	2	$^3P_2$
			1	0	-1			.. .	1	$^3P_1$
				0				.. .	0	$^3P_0$
				0				... . ..	0	$^1S_0$

In a similar manner it may be shown that two equivalent p-electrons (corresponding to the electron configuration p^2) yield the terms $^1S_0$, $^1D_2$, $^3P_2$, $^3P_1$, $^3P_0$. On the other hand, for the case of two non-equivalent p-electrons, the spectral terms are $^1S_0$, $^1P_1$, $^1D_2$, $^3S_0$, $^3P_2$, $^3P_1$, $^3P_0$, $^3D_3$, $^3D_2$, $^3D_1$.

For more than two electrons, the derivation of spectral terms becomes a more tedious task. The results deduced for different configurations are shown in Tables 15.3 and 15.4 which are given by G. Herzberg.[1] The numbers in parentheses indicate the number of corresponding terms. For example $^2P(4)$ means that there are four sets of ^2P terms (that is four terms of type $^2P_{1/2}$ and four of type $^2P_{3/2}$.

In the case of *closed shells*, that is those which contain their maximum number of electrons, $S = 0$, since all the electrons are paired. Furthermore, since

TABLE 15.3

TERMS OF NON-EQUIVALENT ELECTRONS

Electron Configuration	Terms
ss	^1S, ^3S
sp	^1P, ^3P
sd	^1D, ^3D
pp	^1S, ^1P, ^1D, ^3S, ^3P, ^3D
pd	^1P, ^1D, ^1F, ^3P, ^3D, ^3F
dd	^1S, ^1P, ^1D, ^1F, ^1G, ^3S, ^3P, ^3D, ^3F, ^3G
sss	^2S, ^2S, ^4S
ssp	^2P, ^2P, ^4P
ssd	^2D, ^2D, ^4D
spp	^2S, ^2P, ^2D, ^2S, ^2P, ^2D, ^4S, ^4P, ^4D
spd	^2P, ^2D, ^2F, ^2P, ^2D, ^2F, ^4P, ^4D, ^4F
ppp	$^2S(2)$, $^2P(6)$, $^2D(4)$, $^2F(2)$, $^4S(1)$, $^4P(3)$, $^4D(2)$, $^4F(1)$
ppd	$^2S(2)$, $^2P(4)$, $^2D(6)$, $^2F(4)$, $^2G(2)$, $^4S(1)$, $^4P(2)$, $^4D(3)$, $^4F(2)$, $^4G(1)$.
pdf	$^2S(2)$, $^2P(4)$, $^2D(6)$, $^2F(6)$, $^2G(6)$, $^2H(4)$, $^2I(2)$
	$^4S(1)$, $^4P(2)$, $^4D(3)$, $^4F(3)$, $^4G(3)$, $^4H(2)$, $^4I(1)$

[1] Ref., G. H., p. 132.

TABLE 15.4

TERMS OF EQUIVALENT ELECTRONS

Electron Configuration	Terms
s^2	^1S
p^2	^1S, ^1D, ^3P
p^3	^2P, ^2D, ^4S
p^4	^1S, ^1D, ^3P
p^5	^2P
p^6	^1S
d^2	^1S, ^1D, ^1G, ^3P, ^3F
d^3	^2P, $^2D(2)$, ^2F, ^2G, ^2H, ^4P, ^4F
d^4	$^1S(2)$, $^1D(2)$, ^1F, $^1G(2)$, ^1I, $^3P(2)$, ^3D, $^3F(2)$, ^3G, ^3H, ^5D
d^5	^2S, ^2P, $^2D(3)$, $^2F(2)$, $^2G(2)$, ^2H, ^2I, ^4P, ^4D, ^4F, ^4G, ^6S

in a closed shell all the orientations possible in a magnetic field are present, $\Sigma m_0 = M_L = 0$. Hence $J = 0$, and the spectroscopic term is therefore of type $^1S_0$.

Thus as shown in Table 13.2, atoms of the elements of Groups 0 and 2, in which there are two s-electrons in the valence shell, and of palladium (in which the d-shell is filled) all exhibit in the normal state spectroscopic terms of type $^1S_0$. It follows that in deriving the spectral term of a many-electron atom, we need consider only those electrons which are in incomplete shells. For instance, in the case of Si ($Z = 14$) for which the electron configuration is $1s^2 2s^2 2p^6 3s^2 3p^2$, we need consider only the interaction of the two $3p$ electrons.

Another important conclusion is that if N_e denotes the maximum number of electrons for any one type of level ($N_e = 2$ for s, $N_e = 6$ for p, $N_e = 10$ for d levels, and so forth) then the spectral terms for $N_e - n$ electrons are the same as those for n electrons. Thus, the spectral terms for the configuration p^2 are the same as for p^4. The only difference occurs in the order of multiplet levels with respect to the value of the energy. While in the case of the p^2 configuration the lowest level is of type $^3P_0$, the lowest level for the p^4 configuration is $^3P_2$, as shown in Table 15.5.

TABLE 15.5

TERMS FOR EQUIVALENT p-ELECTRONS

Number of Electrons	Terms	Normal Term
1	^2P	$^2P_{1/2}$
2	$^1S_0$ $^1D_2$ ^3P	$^3P_0$
3	^2P ^2D ^4S	$^4S_{3/2}$
4	$^1S_0$ $^1D_2$ ^3P	$^3P_2$
5	^2P	$^2P_{3/2}$
6	$^1S_0$	$^1S_0$

In order to draw attention to the origin of a particular energy level the term symbol is often preceded by the symbol for the electronic configuration, as shown in the following examples:

He: $1s^2\ {}^1S_0$ (lowest term), $1s2p\ {}^3P_{2,1,0}$ (excited state);

Tl: $6s^2 6p\ {}^2P_{1/2,\ 3/2}$ (lowest terms);

Ti$_{\rm I}$: $3d^2 4s^2\ {}^3F_{2,3,4}$; $3d^3 4s\ {}^5F_{1-5}$ (excited state);

Ti$_{\rm II}$: $3d^2({}^3F)4s\ {}^4F_{3/2-9/2}$ (normal state),

$3d^3\ {}^4F_{3/2-9/2}$ (excited state).

These symbols indicate, for instance, that the excited state in Ti$_{\rm I}$ is obtained by exciting one of the $4s$ electrons to state $3d$; and in the case of Ti$_{\rm II}$, the normal term is derived from the ${}^3F$ state of Ti$_{\rm I}$ by removal of one of the $4s$ electrons. This method of describing the nature of energy levels is especially useful in the case of stripped atoms and more complex electronic configurations.

In X-ray spectral levels we have another illustration of the deduction that spectral terms for $N_e - n$ electrons in a shell are the same as those for n electrons. Thus, as shown in Table 14.2, the $L_{\rm I}$ level which has the configuration $(2s)(2p)^6$ has the same spectral type of term as a $2s$ orbital while the $L_{\rm II}$ and $L_{\rm III}$ levels which are associated with the configuration $(2s)^2(2p)^5$ are of the same spectral type as those observed for a $2p$ orbital (when electron spin is taken into account).

In the case of atoms with single valence electrons, as in the alkali elements, the *normal term*, or term corresponding to the lowest energy state, is of type ${}^2S_{1/2}$, and for atoms with two equivalent s-electrons (as in helium and elements of Group II) the normal term is of type ${}^1S_0$.

For electronic configurations containing equivalent p- or d-electrons the normal term is determined in accordance with the following two rules, originally suggested by Hund:

(1) The normal term is that with highest value of the multiplicity r.

(2) For atoms in which the valence shell contains less than half the maximum number of electrons the deepest component of a multiplet is that for which $J = L - S$, that is, J has the lowest possible value. Such multiplets are known as *regular*.

(3) When the shell is more than half filled, the component of the multiplet which has lowest energy is that for which $J = L + S$, that is, J has the highest value. Such multiplets are designated as *inverted*.

In Tables 15.3 and 15.4 the normal term associated with a given configuration is the one mentioned last. Table 15.5 illustrates rules (2) and (3) for the order of the multiplets.

The *normal terms* for the different atomic systems are given in the second last column of Table 13.2. Not only do they illustrate the application of the rules mentioned above, but they demonstrate that, as in every other respect,

the periodicity of the elements is exhibited in both electronic configuration and spectral behavior.

With regard to most of the rare-earth elements ($Z = 57$ to $Z = 71$) and some of the elements of still higher atomic number there seems to be some question at present regarding the spectral type of the normal term.[1]   Undoubtedly this is due to the extreme complexity of the spectra, as indicated by the occurrence of spectral terms which are characterized by large values of both S and L.

In concluding this section it is essential to point out that while the Russell-Saunders coupling has been used in the discussion so far, this is not the only type of coupling which is possible.   This procedure is strictly justified only for cases in which the interaction of the individual l-vectors and individual s-vectors is so strong that they give rise to resultant L and S vectors.   "This assumption," as Herzberg states,[2] "holds for a large number of elements, particularly for all the lighter elements, as may be seen from the fact that, for them, the multiplet splitting is usually small compared to the energy difference of the levels having the same electron configuration but different L.   The splitting is likewise small compared to the energy differences of corresponding levels which differ only in their multiplicities."

If, however, it is assumed that the spin-orbit interaction for each electron is much stronger than any l-l or s-s interaction, we obtain the so-called jj coupling.   This may be represented symbolically by the relation

$$(l_1 s_1)(l_2 s_2) \cdots = (j_1 j_2 j_3 \cdots) = J, \qquad (15.11)$$

which should be compared with equation (15.9) stated near the beginning of this section.   Each l_i and s_i combine to form a vector j_i, and these then combine to form a resultant J.   While this procedure yields definite values for J and M, L and S remain indefinite.   A detailed consideration shows that while the number of terms is the same as for the LS coupling, the separations are not the same, since the mode of interaction of individual electrons is just the opposite of that involved in LS coupling.   Furthermore, since L and S are no longer definite, it is impossible to apply the selection rules for these quantum numbers.   The only selection rules applicable in these cases are $\Delta J = 0, \pm 1$, and $\Delta j_i = 0, \pm 1$.

As might be expected from the fact that LS and jj coupling represent two extremes, transition cases occur.   Thus, as the value of Z is increased in the elements of Group IV (C, Si, Ge, Sn, Pb), the coupling changes from pure LS in the first two members to a type which is closer to jj coupling in the case of Pb.[3]

---

[1] The term symbols given in the table are those used by L. P., *op. cit.*   They are different for some of the elements mentioned from those given in a similar table by G. H., *op. cit.*   In fact for many of the rare earth elements, the latter has indicated the lack of information by a blank space.

Op. cit., pp. 173–4.

[3] G. H., *op. cit.*, p. 175.   See also ref., H. E. W., p. 200.

Figure 15.8 [1] shows the ideal vector modes for (A) LS coupling and (B) jj coupling. It will be observed that in (A) the vectors $L^* = \sqrt{L(L+1)}$ and $S^* = \sqrt{S(S+1)}$ precess about their resultant $J^* = \sqrt{J(J+1)}$. (An asterisk is used by White to distinguish the *magnitude* of the vector from the corresponding quantum number.) The particular case illustrated is that for which $L = 3$,
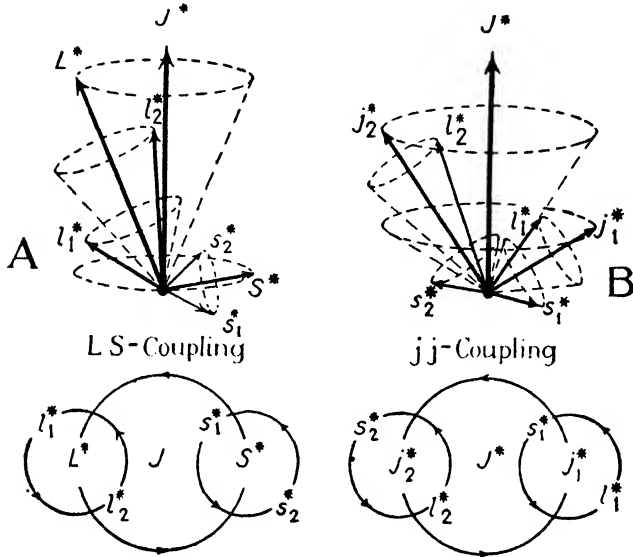
FIG. 15.8.   Ideal Vector Modes for (A) LS-Coupling and (B) jj-Coupling (White)

$S = 1$, and $J = 3$. The angle, θ_1, between the vectors L^* and J^* is given by the trigonometric relation,

$$3(3+1) + 3(3+1) - 2.3(3+1)\cos\theta_1 = 1(1+1).$$

Consequently $\cos\theta_1 = {}^{11}\!/_{12}$, and $\theta_1 = 23°\,36'$. Similarly, we derive the value of the angle θ_2 between L^* and S^*, by the relation,

$$3(3+1) + 1(1+1) + 2\sqrt{4 \times 2}\cos\theta_2 = 3(3+1),$$

which yields the result $\cos\theta_1 = -0.3536$, $\theta_1 = 110°\,42'$.

In case B, the vectors j_1^* and j_2^* are the resultants of $l_1^*s_1^*$ and $l_2^*s_2^*$ interactions respectively, and they precess about their resultant J^*. The angles between the different vectors are deduced by means of trigonometric relations similar to those used above.

Figure 15.9 [1] shows the behavior of the spectral terms in weak magnetic fields (Zeeman effect). In both types of coupling the resultant vector J^*

[1] Ref., H. E. W., *op. cit.*, p. 191.

precesses about its component m in the direction of the field. The particular case illustrated is the same as that shown in the previous figure.

It should be mentioned that in the case of jj coupling, the value of the factor g for the Zeeman effect is calculated by means of a different formula from that used for LS-coupling. However, *Pauli's g sum rule* applies for this case also. This rule states that for all the levels arising from a given electron configuration the sum of the g-factors for levels with the same value of J is a constant, independently of the nature of the configuration.
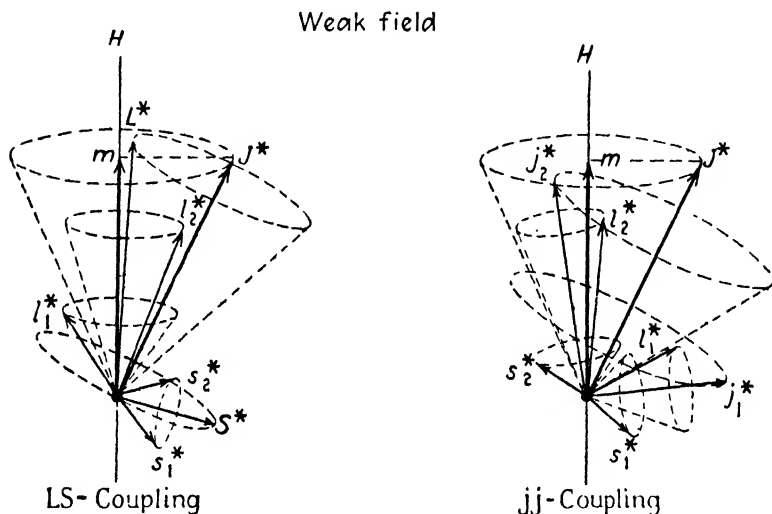
FIG. 15.9.   Illustrating Precession of Vectors in Weak Magnetic Field for LS- and jj-Coupling

(5) **Isoelectronic Sequences:** In Section 13(3), on "Enhanced Spectra," attention was drawn to the similarity in respect to spectral terms of the series of sodium-like atoms Na_I to Cl_{VII}. Such a series of atoms having the same extranuclear electronic configuration is known as an *isoelectronic sequence.* A number of such sequences have been investigated by R. C. Gibbs and H. E. White and Fig. 15.10 [1] shows the regular displacement of multiplets for the normal and stripped atoms in the first and second long periods. The ordinates give the values of $\bar{\nu}$ for the transitions indicated in the center of the figure. Thus the first vertical line gives values of $\bar{\nu}$ for the line $4^2S_{1/2} \rightarrow 4^2P_{1/2}$ (first line of the principal series) for the isoelectronic sequences K_I to Cr_{VI} and Rb_I to Zr_{IV} respectively. The second column gives values of $\bar{\nu}$ for the line $^3D_3 \rightarrow ^3F_4$ in the sequences Ca_I to Cr_V and Sr_I to Cb_V, for which the external configurations are of type $(ns)^2$ This line corresponds to a transition from dp to a ds configuration. In the following columns the transitions considered are those corresponding to $d^ns \rightarrow d^np$, where n varies from 2 to 10.

[1] *Proc. Nat. Acad. Sci.*, **13**, 525 (1927).   See also ref., H. E. W., Chap. XVII.

The figure illustrates the application of the procedure discussed in the previous section for the derivation of spectral terms. Thus, it will be seen that with increasing value of Z, the multiplicity alternates between even and odd, and also that the degree of multiplicity passes through a maximum ($r = 7$)
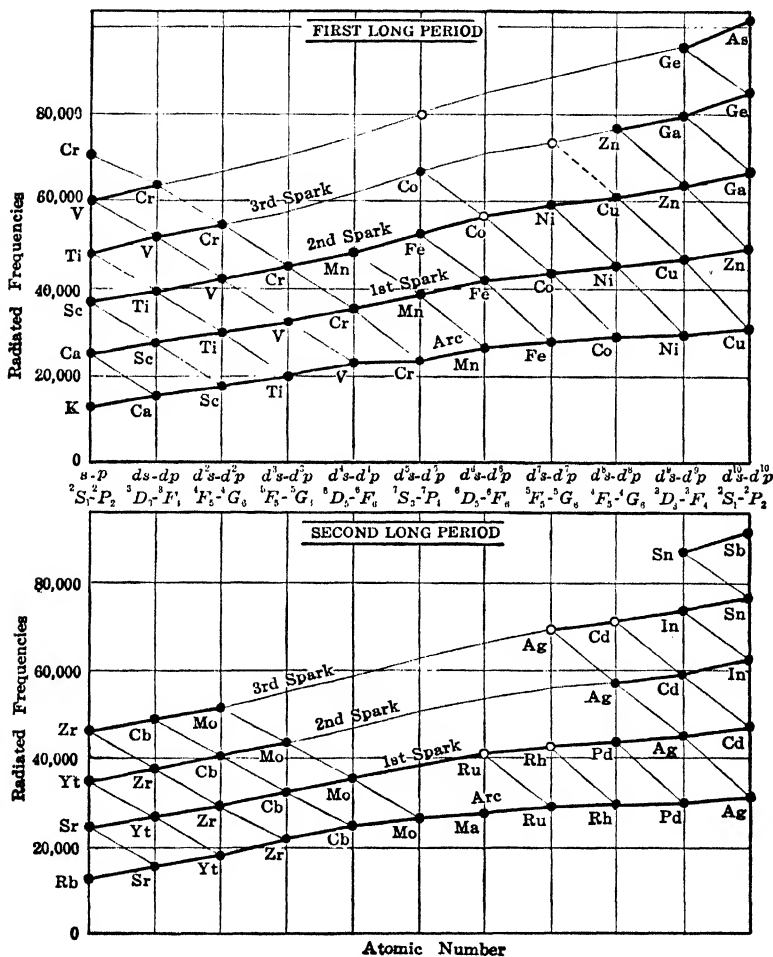
FIG. 15.10. Regular Displacement of Multiplets in Spectra of Atoms of First Two Long Periods

for atoms isoelectronic with Cr_I. It will also be observed that the configurations $d^{10}s$ and $d^{10}p$ yield the same types of spectral terms, respectively, as single s and p electrons, and a similar statement holds valid for configurations involving d^9 and d^8 as compared with those involving d and d^2 respectively.

Figure 15.11 taken from a paper by H. E. White [1] shows Moseley energy level plots for the different isoelectronic systems. The electron configuration corresponding to each set of four heavy diagonal lines is given below each sequence in the order in which they appear for the last elements. It will be observed in the case of the K_I to V_V series that while the order of increase in $\bar{\nu}$ values is $4d$, $3d$, $4p$, $4s$ for K_I, this order is altered in the case of the subsequent elements, so that in V_V the $3d$ level has the highest value of $\bar{\nu}$, "which indicates an increased binding of a $3d$ electron over a $4p$ and a $4s$ electron," as the nuclear charge is increased. In the series Ca_I to Cr_V a similar occurrence is observed.
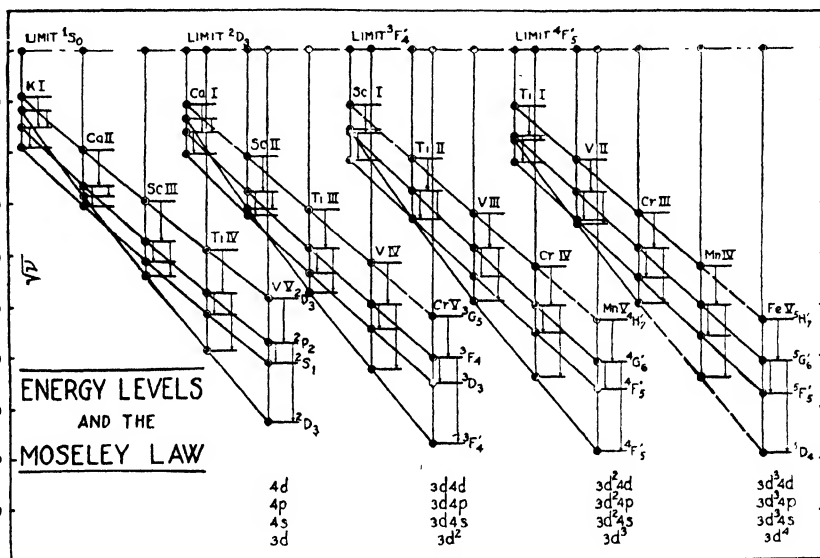
FIG. 15.11.   Moseley Plots for Different Iso-Electronic Systems of First Long Period

The lowest term for Ca_I is the resultant of one electron in a $3d$, and the other in a $4s$ orbit, but in Cr_V the corresponding term is formed by two electrons each of which is in a $3d$ orbit.

The limits for each sequence are indicated at the top of the figure. Thus the limit for the K_I sequence is the lowest term in K_{II} (isoelectronic with Argon), which is of type $^1S_0$ (see Table 13.2). Similarly the limit of the Ca_I sequence is a $^2D_3$ term corresponding to the removal of one of the $4s$ electrons and the binding of the residual electron in a $3d$ orbit. In fact, "the increased binding of the electron configuration $3d^n$ over the electron configurations $3d^{n-1}4s$, $3d^{n-1}4p$, and $3d^{n-1}4d$ (where $n = 1, 2, 3, 4$ for the first, second, third and fourth sequences respectively) appears to be almost identical for each sequence. In going from one sequence to the next (from left to right) the

[1] *Phys. Rev.*, **33**, 914 (1929), Fig. 9.

heavy diagonal line $3d^n$ gradually shifts down with respect to the other three parallel diagonals."

Another interesting feature brought out by the diagram is the parallelism existing between the lines $4s$, $4p$ and $4d$ in the K_I sequence and between similar lines in the other sequences, a regularity which is a result of the *irregular doublet law*. Fig. 15.12 and the following remarks on this figure taken from the same paper by H. E. White emphasize the manner in which this law has been applied in the determination of electron configurations from spectral terms.
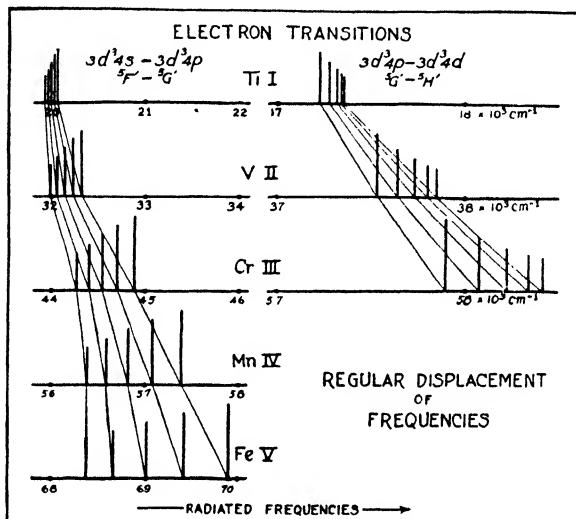
Fig. 15.12. Regular Displacement of Frequencies for Transitions Beteeen Similar Levels

"The irregular doublet law, wherever applicable, proves to be the most powerful method of attack in attempting to analyze the spectra arising from ionized atoms. The irregular doublet law is applicable to those radiated lines arising from electron transitions involving no change in total quantum number. For sequences of isoelectronic systems involving only one valence electron (i.e., K_I, Ca_{II}, etc.) an electron transition gives rise to only two or three radiated lines. In the sequence starting with Ti_I, however, *where four valence electrons are involved, electron transition may give rise to over a hundred radiated lines.*[*] In this report on the latter sequence of isoelectronic systems only a few of the strongest lines have been traced through five elements. For the electron transition $3d^34p$ to $3d^34s$ about forty lines, and for the electron transition $3d^34d$ to $3d^34p$ about twelve lines, have been traced through the first three elements, Ti_I, V_{II}, and Cr_{III}."

The figure shows the regular displacement of frequencies and increasing width of separation of the lines corresponding to these transitions.

Other isoelectronic sequences which have been investigated are the following: Cu_I to Sc_{VI}, by R. A. Sawyer and C. J. Humphreys,[1] N_I to Ge_V, by J. E.

[*] The italics are the present writer's.

[1] *Phys. Rev.*, **32**, 583 (1928).

Mack, O. Laporte and J. R. Lang,[1] Ni_I to Kr_{IX} and Pd_I to Xe_{IX} by P. G. Kruger and W. E. Shoupp,[2] Cl_I to Mn_{IX} by P. G. Kruger and L. W. Phillips,[3] A_I to Fe_{IX} by the same investigators and S. G. Weissberg[4] and Br_I to Sr_{IV} by D. H. Tombourian.[5] In all these case Moseley plots similar to those shown in Fig. 15.11 have been obtained.

It is of interest in this connection to observe the progress that has been made in the analysis of ordinary and enhanced spectra since about 1930.   A. G. Shenstone has pointed out in a review published in 1938,[6] that, while Bacher and Goudsmit's "Atomic Energy States," published in 1932, listed spectral terms for 231 normal and stripped atoms, there were available at the time he wrote his report, analyses of 169 more spectra.   A considerable number of these analyses refer to spectra of atoms which have been stripped of more than 7 electrons.   For instance, the Neon sequence has been extended to Cr_{XV}, and other sequences have been extended to ten or more members.   In a more recent review of "Spectroscopy in the Vacuum Ultraviolet," J. C. Boyce[7] has listed 31 isoelectronic sequences in the ultraviolet, which include not only those mentioned above, but also additional observations made since 1938.

Even in the analysis of spectra of rare earth elements progress has been made.   As is evident from the spectral notation of the normal terms for these elements, given in Table 13.2, these spectra are extremely complex.   The difficulties in deriving spectral terms for atoms of this group may be realized better when one considers that in such a relatively simple case as that of titanium, the systems of terms present in the successive spark spectra are as follows.[8]

	Ti_I	Ti_{II}	Ti_{III}	Ti_{IV}
Electron configuration:	$3d^2 4s^2$	$3d^2 4s$	$3d^2$	$3d$
Systems in spectrum:	$\left\{\begin{array}{l}\text{Singlets}\\\text{Triplets}\\\text{Quintets}\end{array}\right.$	$\left\{\begin{array}{l}\text{Doublets}\\\text{Quartets}\end{array}\right.$	$\left\{\begin{array}{l}\text{Singlets}\\\text{Triplets}\end{array}\right.$	Doublets

Several factors have contributed towards this progress in analysis of spectra. The introduction of the grazing-incidence grating spectrograph has made possible the photography of "optical" lines down into the region of soft X-rays.[9]   For instance, V_i for Cr_{XV} is over 1000 volts, and the corresponding lines are as short as 18.5 Å units.   This has been of special importance in the

[1] *Ibid.*, **31**, 748 (1928), also J. E. Mack, *ibid.*, **34**, 17 (1929).

[2] *Ibid.*, **46**, 124 (1934).

[3] *Ibid.*, **51**, 1087 (1937).

[4] *Ibid.*, **51**, 1090 (1937).

[5] *Ibid.*, **54**, 350 (1938).

[6] *Reports on Progress in Physics*, **5**, 210 (1938).   This paper gives a bibliography of papers on spectroscopy during the period 1934–1938.

[7] *Rev. Mod. Phys.*, **13**, 1 (1941).

[8] H. N. Russell and R. J. Lang, *Astrophys. J.*, **66**, 13 (1927); H. N. Russell, *ibid.*, **66**, 283, 347 (1927).

[9] Discussed in review by M. Siegbahn, *Ergeb. exakten Naturwiss.*, **16**, 104 (1937).

study of higher spark spectra, which was initiated by R. A. Millikan and I. S. Bowen, about 1924. The lines in spectra of stripped atoms such as Cl$_{III}$, Ne$_{IV}$, and so forth, are in the extreme ultraviolet and a refined technique had to be developed for measuring these wave lengths. The analysis of these spectra has been made possible by application of the X-ray doublet laws, mentioned in Section 14(2).

Furthermore, the analysis of very complex spectra would be a prodigious labor if unassisted by the mechanical means devised by G. R. Harrison and his associates.[1]

(6) **Ionizing Potentials of Normal and Stripped Atoms:** In Sections 1(3) and 1(4) the ionization potential (V_i) has been defined as the energy required to remove one of the optical or valence electrons completely from the normal level, while the resonance potential (V_r) is defined as the energy required to transfer an electron from the normal to the first excited state. These potentials may be calculated by the relation

$$V \text{ (in volts)} = \frac{\tilde{\nu}_n - \tilde{\nu}_e}{8068}$$

where $\tilde{\nu}_n$ and $\tilde{\nu}_e$ are the wave numbers of the normal and excited levels respectively. In the case of the ionization potentials, $\tilde{\nu}_e = 0$.

While this is the most accurate method for the determination of these *critical potentials* for all those cases in which the levels have been determined from an analysis of the spectral lines, other methods have been used to supplement the spectroscopic method, as mentioned in the sections referred to above. In fact, in the case of some of the more complex atoms, the direct method of measuring V_i by bombardment of the vapor with electrons of definite velocity has been the only one available.

In the case of one-electron and two-electron configurations, where the ionization process involves the removal of an s-electron, the ionization potentials have perfectly definite values, but in the case of more complex configurations there exist more than one value of V_i, depending upon the type of electron removed. This has been emphasized by Millikan and Bowen [2] and also by H. N. Russell.[3]

"In considering ionization potentials," Millikan and Bowen remark, "it should not be overlooked that, *unless there has been careful definition, the term ionizing potential has no meaning at all.* Thus the normal oxygen atom has two electrons in s-orbits and four in p-orbits, and this configuration is therefore designated as the s^2p^4 configuration; but this configuration has triplet P, singlet D and singlet S terms, which correspond to five different orientations of the orbits and the spins of the four p electrons. When one of these p electrons is removed, the atom, now an ion, having left two s and three p electrons, may in its turn exist in any one of

[1] These methods are described in *J. Opt. Soc. Am.*, **25**, 169 (1935), and *Rev. Sci. Inst.*, **9**, 15 (1938). The data are contained in M. I. T. Wave Length Tables, John Wiley and Sons, Inc., New York, 1939.

[2] *Proc Nat. Acad. Sci.*, **13**, 531 (1927).

[3] *Astrophys. J.*, **66**, 233 (1927).

five different states, namely a quartet S, a doublet P, and a doublet D, *so that the atom can be ionized in twenty-five different ways, each of which requires a slightly different energy and hence represents a different ionization potential from all the others.* 'Ionization potential,' therefore, has no definite significance, unless it is defined, for example, as the energy corresponding to the passage from the most stable state of the atom to the most stable state of the ion."

It is this definition which has been used by Millikan and Bowen and practically all other investigators in this field, so that it is the one adopted in the present section.

H. N. Russell has discussed in considerable detail the ionization potentials of elements of the second long period (K to Ni). If we designate the number of electrons outside the "argon shell" by n, the normal state of the atom corresponds to the configuration s in the case of K and $d^{n-2}s^2$ in all the other cases (except Cr for which the normal configuration is d^5s).

Now, as is evident from Table 11.4 the degree of multiplicity, r, changes by $+1$ or -1 as we pass from one element to the next in the periodic arrangement (Heisenberg's "branching" rule). Therefore, in the removal of one of the $4s$ electrons from the configuration $d^{n-2}s^2$ the resulting ion may have a greater or less multiplicity than the neutral atom. Corresponding to these two possibilities we have two different ionizing potentials:

> A: $d^{n-2}s^2$ to $d^{n-2}s$ (greater multiplicity),
> B: $d^{n-2}s^2$ to $d^{n-2}s$ (smaller multiplicity).

Thus in the case of Ca the normal level is of type $^1S_0$. On ionization there results a potassium-like ion, in which the lowest term is of greater multiplicity, i.e., of type $^2S_1$. On the other hand, the ionization may be accompanied by the simultaneous transition of the second electron from the $4s$ to the $3d$ level, and again the multiplicity may be either increased or decreased, with the corresponding two possible ionizing potentials for the normal atoms:

> C: $d^{n-1}s$ (greater multiplicity) to d^{n-1},
> D: $d^{n-1}s$ (smaller multiplicity) to d^{n-1}.

Russell therefore defines the *principal ionizing potential* as that which represents the difference in *energy between the normal states of the atom and that of the ion*. He furthermore accounts for the difference between the four ionizing potentials A, B, C and D as follows:

The differences between the ionization potentials A and B, or C and D admit of a simple explanation: The reverse process for the transition C and D, whether in the arc or the spark, consists of adding a $4s$ electron to a partially completed shell of $3d$ electrons. In case C, the multiplicity is increased, that is, the added electron is *spinning in the same direction* as the resultant spin of those already present. In case D, it is spinning in the opposite direction. Now, as Hund has pointed out, the magnetic interaction produces attraction in the first case, and repulsion in the second, so that the energy of binding is greater for C than for D.

In the case of the ionized atom there may exist three ionizing potentials corresponding to the following processes:

C: $d^{n-2}s$ (greater multiplicity) to d^{n-2},
D: $d^{n-2}s$ (smaller multiplicity) to d^{n-2},
E: d^{n-1} to d^{n-2}.

As an illustration, the following diagram indicates the terms in the spectra of Mn, Mn$_I$ and Mn$_{II}$, and their different modes of formation.
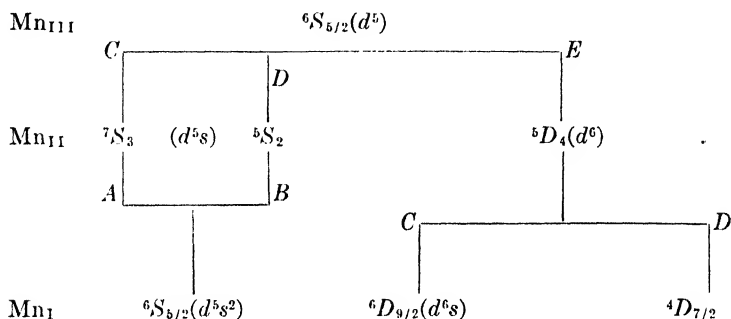

Table 15.7 [1] gives the various ionization potentials of the atoms K to Ni and of the corresponding ionized atoms, classified according to the transitions mentioned above. The last column in each half of the table gives the *principal ionization potential*.

TABLE 15.7

IONIZATION POTENTIALS OF ATOMS AND SINGLY IONIZED ATOMS OF FIRST LONG PERIOD (RUSSELL)

Element	Neutral Atom					Ionized Atom			
	A	B	C	D	Principal	C	D	E	Principal
K.			4.30		**4.32**				
Ca.	6.21		5.39	5.22	**6.09**	11.83		10.13	**11.82**
Sc . .	6.57	6.88	5.74	5.33	6.57	12.80	12.49	12.19	12.80
Ti.	6.79	7.39	6.10	5.48	**6.80**	13.60	12.99	13.45	13.60
V.	7.04	7.84	6.46	5.68	6.76	14.4	13.5	14.7	14.7
Cr.	7.28	8.21	6.70	5.76	**6.74**	15.1	14.1	16.6	16.6
Mn.	7.38	8.55	7.06	6.28	**7.40**	15.7	14.5	13.8	15.7
Fe.	7.83	8.81	7.20	6.58	7.83	16.5	15.4	16.3	16.5
Co.	8.25	9.0	7.38	6.90	7.81	16.8	16.0	17.2	17.2
Ni.	8.65	9.30	7.62	7.22	7.64	17.15	16.5	18.2	18.2
Cu.	8.95	9.48	7.63		7.69	17.62	17.09	20.34	20.34
Zn	9.40				**9.36**	17.93			**17.89**

[1] H. N. Russell, *Astrophys. J.*, **66**, 233 (1927).

The values in heavy type are derived from longer series and are therefore preferred by Russell. It will be seen from this table that the principal potentials for Ca, Sc, Ti, Mn, Fe and Zn correspond to a transition of type A; while those for K, Cr and Cu correspond to a transition of type B. For V, Co and Ni the transition involving the least energy change is of type C.

In this case the transition involves the simultaneous removal of one $4s$ electron and the shift of another from $4s$ to $3d$.

The last column of Table 13.2 gives, as far as possible, the values for each element of the principal ionizing potential as defined by Russell. These values are based largely upon the values published by R. F. Bacher and S. Goudsmit [1] for the wave numbers of the normal terms [2] and on the more recent table of values of V_i for normal and stripped atoms given by G. Herzberg. [3] Values which according to the latter are uncertain are indicated by $\sim$. The values in brackets, are omitted in both the above-mentioned publications and are taken from other sources. [4] There is probably considerable doubt regarding their reliability. [5]

It is of interest to observe that helium has the highest, and cesium the lowest value for the ionizing potential. This is in accordance with the chemical behavior of these two elements. In a general way it may be stated that the ionizing potential tends to increase as the number of electrons in any given level is increased and reaches a maximum value when the particular level is completely filled. Thus the elements of Group 0 have the highest ionizing potentials, and it will be found that the ionizing potential increases as we pass from Li to Be, Na to Mg, K to Ca and Cu to Zn (corresponding to completion of the s-group). On the other hand, the presence of a single electron in a new "shell" leads to a decrease in the value of V_i as compared with those for elements either immediately preceding or following. This is well illustrated in the case of the alkali metals for which the values of V_i are lower than those of the other elements, and also in the case of the triads, Be, B, C; Mg, Al, Si; Zn, Ga, Ge; Cd, In, Sn; Hg, Tl, Pb, in each of which the value of V_i is a minimum in the middle of the group, (corresponding to the presence of one p-electron).

In contrast with this is the observation that in each of the series Ca-Ni, Sr-Pd, and (probably) Ce-Hf, the values of V_i exhibit no striking variation with

---

[1] Ref. B. G.

[2] Since Bacher and Goudsmit (as well as Herzberg) use the factor 8106 for converting volts into wave numbers whereas the value of this factor, on the basis of revised values of e and h, should be 8068, the values for V_i as given in Table 13.2, and calculated from the wave numbers of the normal terms, are 0.5 percent approximately higher than those given in the treatises mentioned.

[3] G. H., *op. cit.*

[4] H. N. Russell, *Astrophys. J.*, **70**, 11 (1929); A. A. Noyes and A. O. Beckman, *Chem. Rev.*, **5**, 85 (1928).

[5] The value of V_i for Ir is given by W. Albertson, *Phys. Rev.*, **54**, 183 (1938) and that for Eu, by H. N. Russell and A. S. King, *Astrophys. J.*, **90**, 155 (1939). They conclude that the lowest term for the latter is of type $f^7s^2 \, {}^8S_0$.

increase in atomic number. This is obviously in agreement with the conclusion that in each of these series increase in nuclear charge is accompanied by addition of an electron to a shell which is within an *already completed* shell.

Next in interest to the problem of ionization potentials of the normal atoms themselves comes that of the ionization potentials of the atoms which

TABLE 15.8

Element	Z	Config. of outer electrons	Electron Volts for Removal of Outer Electron from				
			M	M^+	M^{2+}	M^{3+}	M^{4+}
H	1	$1s$	13.595				
He	2	$1s^2$	24.58	54.38			
Li . .	3	$2s$	5.39	75.62	122.4		
Be	4	$2s^2$	9.32	18.21	154.8	217.7	
B	5	$2s^2 2p$	8.32	25.12	37.93	259.3	340.1
C	6	$2s^2 2p^2$	11.26	24.39	47.88	64.5	392.0
N	7	$2s^2 2p^3$	14.55	29.61	47.63	77.	97.9
O	8	$2s^2 2p^4$	13.61	35.10	55.14	77.4	113
F	9	$2s^2 2p^5$	17.42	34.97	62.65	87.1	114.2
Ne .	10	$2s^2 2p^6$	21.56	40.1	63.5	—	—
Na . . .	11	$3s$	5.14	47.27	71.04	—	—
Mg	12	$3s^2$	7.64	15.03	80.08	109.4	—
Al	13	$3s^2 3p$	5.99	18.82	28.44	119.9	154.1
Si	14	$3s^2 3p^2$	8.15	16.34	33.50	45.1	166.3
P	15	$3s^2 3p^3$	10.95	19.65	30.13	—	55.0
S	16	$3s^2 3p^4$	10.35	23.4	35.06	47.3	63
Cl	17	$3s^2 3p^5$	13.01	23.78	39.87	53.38	67.7
A	18	$3s^2 3p^6$	15.76	27.88	40.93	~61	~78
K	19	$4s$	4.34	31.80	46.7	—	—
Ca	20	$4s^2$	6.11	11.87	51.18	70.0	—
Sc	21	$4s^2 3d$	6.7	~12.8	24.72	~73.9	97.5
Ti	22	$4s^2 3d^2$	6.83	~13.6	~27.6	43.16	~99.6

are singly, and, more generally, multiply ionized. In previous sections, the results of investigations on enhanced spectra have been discussed at length. In the present connection we shall consider the relations which have been observed for the ionizing potentials of isoelectronic systems and also the manner in which the ionizing potential varies as successive electrons are removed from the same atom.

Table 15.8 taken, with slight modifications, from a similar table given in

the book by G. Herzberg,[1] gives ionization potentials for the normal and ionized states of the elements $Z = 1$ to $Z = 22$.

These values are based to a large extent upon the observations on iso-electronic sequences mentioned in the previous section as well as on the observations on enhanced spectra of a number of elements. For instance terms in the spectra of F_{II}, F_{III} and F_{IV} as well as those of Cl_{III}, Cl_{IV}, and Cl_V have been derived by I. S. Bowen [2] from observations on wave lengths in these spectra in the extreme ultraviolet region.

In Table 15.8 a stair-like line has been drawn to the right of those values which correspond to the complete removal of the electrons in the valence shell, the configuration of which is indicated in the third column. This line thus represents the direction along which are arranged different isoelectronic sequences. For instance, immediately above the uppermost of the heavy lines are arranged the members of the sequence which are isoelectronic with Li_{II}, and immediately below the line the members of the series isoelectronic with Li_I.

Since the individual values refer to the energy of removal of an electron from those still present in the outer shell at that stage, the energy for the removal of *all* the electrons in a given configuration is the sum of these values. A better conception, from the point of view of the chemist, is obtained by converting these results into gram-calories per gram-atom.[3]

Thus, in the case of beryllium, the total energy required for the removal of the electrons from the 2s- and 1s-shells is as follows:

Original Electron Configuration	Energy in kcal. gm.-atom $^{-1}$ for removal of one electron	Total Energy in	
		Volts	kcal. gm.-atom $^{-1}$
$1s^2 2s^2$	214.9	9.32	214.9
$1s^2 2s$	419.0	27.53	633.9
$1s^2$	3541	181.3	4175
$1s$	5012	399	9187

The last column gives the *total energy* required for the removal of 1, 2, 3 or 4 electrons respectively. It will be observed that the energy required for the removal of the K-electrons is considerably greater than that required to remove the two outer electrons.

Comparing with these values the chemical energy of formation of $BeCl_2$, 155 kcal. per gram mole, it is seen that in general the energy of removal of one electron from the valence shell is of the same order of magnitude as chemical

---

[1] *Op. cit.*, pp. 200–201. The values given in this table have been increased in the ratio 8107/8068 to take into account the revised values of h and e. See also Gasentladungstabellen, M. Knoll, F. Ollendorf and R. Rompe, Julius Springer, Berlin (1935).

[2] *Phys. Rev.*, **45**, 82, 401 (1934).

[3] The conversion factors are given by the relations: 1 electron volt = 23,055 cal. gm.-atom^{-1} volt^{-1} and 10^8 cm.$^{-1}$ = 2.858 kcal. gm.-atom^{-1}.

heats of formation, while that required for the removal of two or more electrons is usually larger than any chemical energy of formation. Furthermore, the energy required to remove electrons from the rare gas shells underneath the valence shells is of a much different order of magnitude.

The most striking feature about these data is the observation that if we plot the square roots of the values of V_i (or $\sqrt{\bar{\nu}/R}$) corresponding to stripped atoms which are isoelectronic, against Z, approximately straight lines are obtained. Fig. 15.13 shows a series of such lines plotted for the series Li
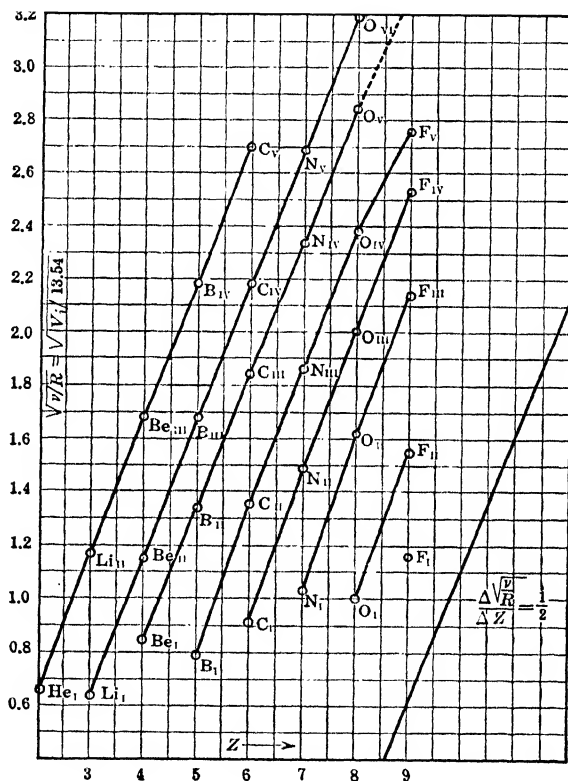
Fig. 15.13.   Moseley Plots for Ionization Potentials of "Stripped" Atoms

to F in all the states of ionization. Values for O_{VI} and F_{VII} have been obtained from data published by Millikan and Bowen. The regularity of the lines furnishes a beautiful illustration of the validity of Moseley's law for isoelectronic systems. As a matter of fact, the Moseley diagram in Fig. 14.4 for the $3s$ level in the series Na_I to S_{VI} represents a plot of the same data, since in the case of these one-electron systems this level is the lowest, and therefore corresponds to the ionizing energy. Furthermore, a comparison with the slope

of the line for which $\dfrac{\Delta\sqrt{\bar\nu/R}}{\Delta Z} = \frac{1}{2}$, is evidence, as in the case of the K levels for elements of high atomic number, that the total quantum number for these levels is equal to 2.

It will also be observed that the Moseley line shown in Fig. 15.13 for the series He$_I$, Li$_{II}$, Be$_{III}$, B$_{IV}$ and C$_V$ (in all of which the electron removed belongs to the He shell) [1] has a slope which is *exactly twice that for the series* Li$_I$ to O$_{VI}$. (In the diagram the slopes actually appear the same because the values of $(\frac{1}{2})\sqrt{\bar\nu/R}$ have been plotted.) *This again is in agreement with the conclusion that in these atoms the electrons are in the* 1s *level.*

For the elements of the series beginning with Na, we find relations between the different ionizing energies similar to those observed for the first series.
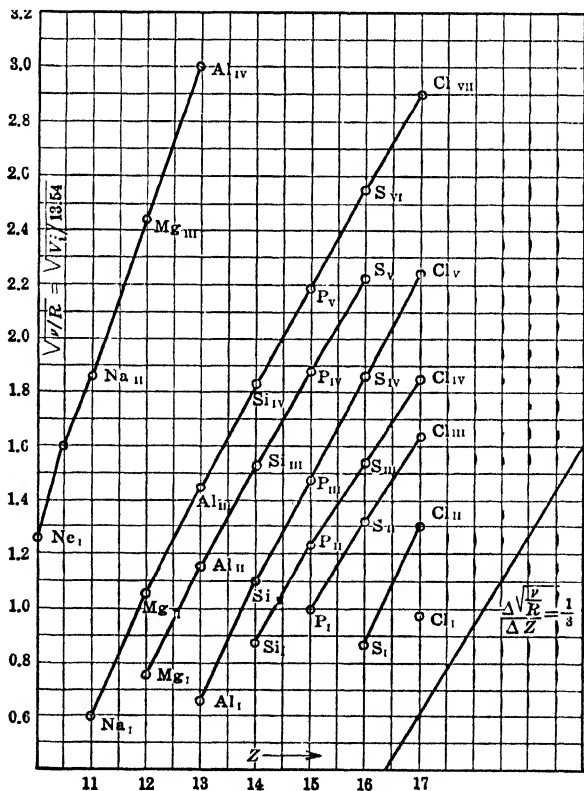
Fig. 15.14.   Moseley Plots for Ionization Potentials of "Stripped" Atoms of Series Na to Cl.
In these plots ν = wave number

[1] More recent term values for the members of this series, including N$_{VI}$ and O$_{VII}$, are given by H. A. Robinson, *Phys. Rev.*, **51**, 14 (1937).

The Moseley diagrams for isoelectronic systems are shown in Fig. 15.14. The slope is not as well defined, but is approximately $\frac{1}{3}$, and here it is also observed that the values for the series Ne_I to Al_{IV} (which is analogous to the series He_I to C_V) shows the slope $\frac{1}{2}$, indicating that the electrons in these systems are in levels for which the total quantum number is 2, whereas in the systems $Na_I - Cl_{VII}$, etc. the electrons are in $3s$ levels corresponding to the value $\frac{1}{3}$ for the slope.

(7) **Application of Wave Mechanics to the Many-Electron Atom:** In Section 15(2) we considered briefly the wave mechanics treatment of the helium atom problem, and in the subsequent sections there were discussed the methods by which the type of spectral terms may be deduced for a given electron configuration. It is of interest in this connection to discuss somewhat qualitatively the methods used and results obtained in the application of quantum mechanics to the problem of the many-electron atom.[2]

The Schroedinger equation for a complex atom, has the form

$$\nabla^2\phi + \frac{h^2}{8\pi^2 m}\left\{ E + \sum_{i=1}^{z}\frac{Ze^2}{r_i} - \sum_{i,j}'\frac{e^2}{r_{ij}} \right\}\phi = 0, \tag{15.12}$$

where the first summation corresponds to the attractive energy between the nucleus of charge $+ Ze$ and each of the Z electrons, and the second summation corresponds to the repulsive energy between each pair of electrons. The prime on the second $\sum$ indicates that the combined i, j is taken only for values of $j > i$. For the case $Z = 2$, this equation becomes identical with equation (15.1).

If the so-called "perturbation" terms e^2/r_{ij} were absent, the solution would be the product of Z eigenfunctions, one for each electron. Hence, the important problem in the solution of equation (15.12) is that of taking into account the repulsive terms between the electrons.

Now the total energy, E, may be separated into two parts: one corresponding to the total kinetic energy of the electrons, which we shall designate by T, and the other representing the potential energy, designated by V. Since the electrons are in constant motion, we are interested in the average values, $\bar{T}$ and $\bar{V}$. The latter is the average of the result obtained by adding the two summations in equation (15.12). Since the total energy is negative for a stable system, and $\bar{T}$ is always positive (since it consists of terms like $\frac{1}{2}mv^2$), it follows that $\bar{V}$ must be negative, and greater in absolute magnitude than $\bar{T}$.

Furthermore, for a stable state, E must possess a minimum value. Hence, the proper solution of equation (15.12) must lead to such a value for ϕ as will make E a minimum. That is, the distribution function for the charge density obtained by solving the Schroedinger equation must be of such a form, that E will have a minimum value for this distribution as compared with any other conceivable distribution. In general, the particular form assumed corresponds

approximately to a single-electron function or the product of two or more such atomic orbitals with one or more arbitrary parameters included. The values of these parameters are then determined by the variational method.

Of course, the fact that the value of E thus deduced, by assuming a particular form for ϕ, is a minimum, is no assurance that there does not exist a lower value of E which might be deduced by a better choice for the form of ϕ. The experimental observations on ionization potentials and values of spectral terms in general provide therefore the only criterion by which, ultimately, a decision must be reached regarding the validity of the particular expression chosen for the eigenfunction, ϕ, that is, for the distribution function $|\phi|^2$.

It is essential in this connection to observe that minimizing E involves a minimizing of both $\bar{T}$ and $\bar{V}$. Now E can be decreased (made more negative) by decreasing $\bar{V}$. This means that the distances r_i which enter into the first summation in equation (15.12) must be decreased, and the distances $r_{i,j}$ in the second summation must be increased. Since the contribution to the total potential energy made by the first set of terms constitutes the predominant term in $\bar{V}$, this means that the distribution function will exhibit a decreased extent of the region in which the electrons are confined, on the average. That is, the function $|\phi|^2$ will have the form of a relatively narrow band in the neighborhood of the nucleus, indicating localization of electrons in this region. But in consequence of the Principle of Indeterminism, a decrease in the value of Δx, must be associated with an increase in Δp. Consequently, the kinetic energy, $\bar{T}$, which corresponds to the average of $\sum\limits_{i=1}^{Z} p_i^2/2m$ will be increased.

On the other hand, if we decrease $\bar{T}$, by decreasing the range of values of p_i, then the range of values of r_i must be increased. That is, $|\phi|^2$ assumes the form of a broad band, corresponding to distribution of the electrons over a wide range of values of r_i.

Actually, therefore, a solution must be sought which will be a compromise between these two extremes, and in the case of the hydrogen atom, as indicated in Section 10(1), the correct solution is such that $\bar{T} = -\bar{V}/2$, and $E = \bar{V}/2$.

Of the methods which have been developed for treating the problem of the many-electron atom, that of the "self-consistent field" developed by D. R. Hartree,[1] and that involving antisymmetrical functions, utilized by J. C. Slater[2] are the most important.

Hartree's method may be described briefly (and crudely) thus: the eigenfunction for the system is represented as the product of Z single-electron functions which must satisfy the following condition. The effective field which is in accord with the assumed charge density distribution function for any one electron (that is, represents a solution of the corresponding Schroedinger equation for a given form of the potential energy function) must be consistent

[1] *Proc. Camb. Phil. Soc.*, 24, 89, 111, 426 (1928) and subsequent paper by Hartree and his associates in *Proc. Roy. Soc.*, [A].

[2] *Phys. Rev.*, 34, 1293 (1929); 35, 210 (1930).

with the field deduced from the charge density distribution due to all the other electrons.

The mathematical technique involves extremely tedious calculations, since it is essentially a method of trial and error involving the successive approxima-
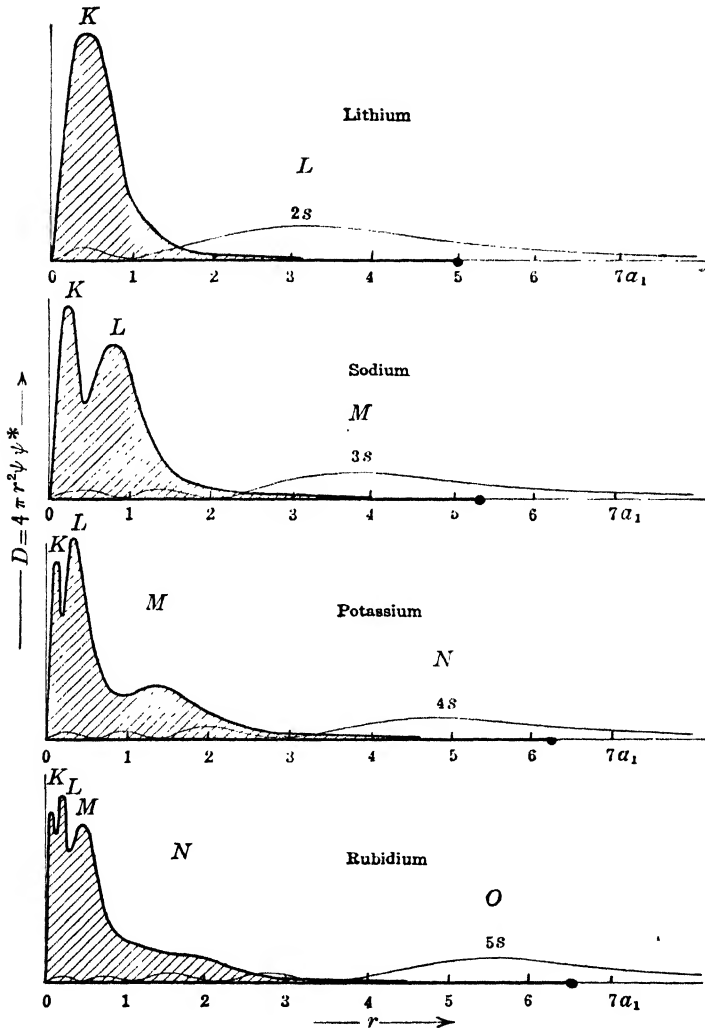

FIG. 15.15.   Probability-Density Distribution Curves for Neutral Alkali Atoms (Hartree)

tion to a more exact result by modifying the form of the eigenfunction used. At each stage of approximation the variational method is used to test the result deduced.

According to Pauli's principle, the complete eigenfunction for any atomic (or molecular) system must be antisymmetrical. Since Hartree's functions do not take this into account, this method is not quite as satisfactory in many cases as that used by Slater. In the latter method the calculation yields relative values of coulomb and exchange energy, and again the variational method is used to test the resulting values for the total energy
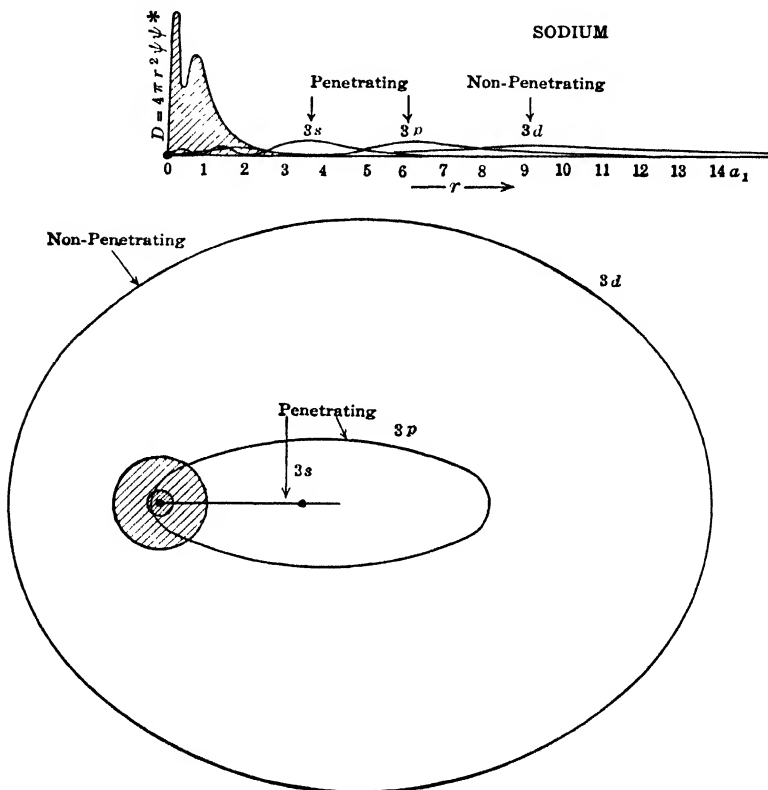
Fig. 15.16. Probability-Density Distribution Curves for Normal and Excited States of Sodium Atom Compared with Bohr-Sommerfeld Orbits for Same States

Figure 15.15 [1] shows probability-density distribution curves for the neutral alkali atoms, as deduced by the Hartree method. The distribution due to inner electrons is indicated by the shaded area, and that due to the valence electron by the curve which extends to the extreme right. The curves indicate not only the presence of the K-, L- and M-"shells," but also the penetration of the "valence" s-type electron into these inner shells. Fig. 15.16 [2] shows the

[1] From ref. H. E. W., p. 101.
[2] *Idem, ibid.*, p. 103.

distribution functions for the valence electron in sodium for the successive states of excitation ($3p$ and $3d$) as deduced by wave mechanics and, for comparison, the Bohr-Sommerfeld orbital model. This figure thus emphasizes the difference between penetrating and non-penetrating orbits which, as mentioned in a previous section, was deduced from the older point of view.

As an illustration of the degree of exactness with which ionization potentials may be calculated from purely theoretical considerations, the investigation of J. Wilson [1] may be mentioned. He has calculated the charge density distribution functions for the isoelectronic sequence Li_I to C_{IV} and deduced values for V_i which are within less than 1 per cent of those observed from spectroscopic data.

For complex atoms containing more than two electrons in the valence shell, the calculation of charge distribution functions and energies for different states becomes even more difficult.

However, as has been pointed out in the discussion of the laws for irregular and regular doublet levels, it has been found possible by the methods of wave mechanics to derive expressions for the energy-differences between spectral terms. Similarly, as shown by R. F. Bacher and S. Goudsmit,[2] it is possible to develop approximate relations between the values of the energy states of an atom and those of the corresponding ion.

(8) **Interval Rules for Multiplets:** In previous sections the interval rules for doublets have been discussed in connection with alkali metal and X-ray spectra. Also interval rules were discussed for the splitting up of lines observed in the Zeeman effect. These observations have proved of great importance in the analysis of spectra for the determination of term values, and in a similar manner determinations of the separation for multiplets in more complex spectra have provided significant information for the elucidation of these spectra.

As stated in equation (14.13), the energy due to interaction of the spin and orbital motions of a single valence electron, with quantum numbers n, l and j, is given by the equation

$$\Delta E_{l,\,s} = - \frac{R\alpha^2 ch(Z-\sigma)^4}{n^3 l(l + \tfrac{1}{2})(l + 1)} \cdot \frac{j(j + 1) - l(l + 1) - s(s + 1)}{2}, \quad (15.13)$$

where $R = R_\infty = 109{,}737$ cm.$^{-1}$; $\alpha^2 = 5.325 \times 10^{-5}$ and $(Z - \sigma)$ is the *effective* nuclear charge.

Dividing by hc, this energy, expressed in wave numbers, is

$$\Delta \bar{\nu}_{l,s} = - a \sqrt{l(l + 1)} \sqrt{s(s + 1)} \cos (ls) = - \Gamma, \quad (15.14)$$

where

$$a = \frac{R\alpha^2(Z - \sigma)^4}{n^3 l(l + \tfrac{1}{2})(l + 1)} = \frac{5.844(Z - \sigma)^4}{n^3 l(l + \tfrac{1}{2})(l + 1)} \text{ cm.}^{-1} \quad (15.15)$$

and the expression for cos (ls) is obtained in the same manner as in the deriva-

[1] *J. Chem. Phys.*, **1**, 210 (1933).

[2] *Phys. Rev.*, **46**, 948 (1934).

tion of Landé's *g*-factor from the relation between the vectors l, s and j.   (See equations (12.11) and (12.16).)

The expression

$$\Gamma = a \sqrt{\overline{l(l+1)}} \sqrt{\overline{s(s+1)}} \cos (ls)$$
$$= \frac{a}{2} \{j(j+1) - l(l+1) - s(s+1)\} \qquad (15.16)$$

is usually referred to as the Γ-*factor*.   Evidently, the wave number for any doublet level is given by

$$\tilde{\nu} = \tilde{\nu}_0 - \Gamma, \qquad (15.17)$$

where $\tilde{\nu}_0$ is the value for the center of gravity of the doublet.

Thus for the $^2P_{1/2}$ and $^2P_{3/2}$ terms of an alkali-like atom

$$\tilde{\nu}_{1/2} = \tilde{\nu}_0 + \frac{a}{2} \cdot 2,$$

$$\tilde{\nu}_{3/2} = \tilde{\nu}_0 - \frac{a}{2} \cdot 1.$$

That is, the $^2P_{3/2}$ term lies above (has a *smaller* wave number than) the $^2P_{1/2}$ term, and the total interval between the two terms is $\Delta\tilde{\nu} = (^3\!/_2)a$.

The interaction energy expressed by equation (15.13) corresponds to the mean value of the product of two terms: (a) the angular velocity of precession of the electron about the direction of j, and (b) the projection of the spin angular momentum on l.   This is illustrated by Fig. 11.2 [1] which shows the precession of the electron spin and orbital vectors around their mechanical resultant j.

We shall now consider the extension of this argument to the derivation of an expression for the energy of LS coupling in an atom with two valence electrons.   In this case it is necessary to evaluate the four interaction energies

$$\Gamma_1 = A_1 \sqrt{\overline{s_1(s_1+1)}} \sqrt{\overline{s_2(s_2+1)}} \cos (s_1 s_2),$$
$$\Gamma_2 = A_2 \sqrt{\overline{l_1(l_1+1)}} \sqrt{\overline{l_2(l_2+1)}} \cos (l_1 l_2),$$
$$\Gamma_3 = A_3 \sqrt{\overline{l_1(l_1+1)}} \sqrt{\overline{s_1(s_1+1)}} \cos (l_1 s_1),$$
$$\Gamma_4 = A_4 l_2(l_2+1) s_2(s_2+1) \cos (l_2 s_2).$$

As shown in Fig. 15.8 A, the vectors * s_1 and s_2 precess with fixed angle of inclination around their resultant S, so that Γ_1 may be calculated by application of the cosine law.   Similarly, l_1 and l_2 precess around their resultant L, and Γ_2 may be calculated in the same manner as Γ_1.   "Now L and S," as White states, "precess around their mechanical resultant in just the same way as l and s of a single electron precess around their resultant j.   The interaction

---

[1] See ref. H. E. W., pp. 189–198 for more complete discussion.

* In the following remarks S_1 actually signifies $\sqrt{\overline{S_1(S_1+1)}}$, and a similar notation is used for the other vectors.

energy due to this precession is attributed to the coupling between each electron's l and its own s, Γ_3 and Γ_4." It may be shown that

$$\Gamma_3 + \Gamma_4 = \frac{A}{2} \{ J(J + 1) - L(L + 1) - S(S + 1) \}, \qquad (15.18)$$

where A is a constant of the same nature as A_1, A_2, A_3, A_4 above and a in equation (15.15).

Of the four Γ-factors thus introduced, the most significant contribution to the interaction energy is that made by the last two. Hence equation (15.18) gives the value of the Γ factor for each component of a multiplet level. From this equation it follows that the intervals (usually measured in terms of wave numbers as $\Delta \tilde{\nu}$) between successive components of a multiplet are proportional to successive differences of $J(J + 1)$. Since these differences are proportional to $(J + 1)(J + 2) - J(J + 1) = 2(J + 1)$ it follows that the magnitude of $\Delta \tilde{\nu}$ for two successive values of J is proportional to the larger of the two values of J associated with this interval. This is known as *Landé's interval rule*.

While this rule has been derived for the interaction of two electrons it has been found equally applicable to multiplicities of higher order.

An illustration of this rule is given by Table 15.9 [1] for the terms $^3P - {}^3D$ in the diffuse subordinate series of calcium.

TABLE 15.9

	$^3P_0$		$^3P_1$		$^3P_2$
$^3D_1$	19310.3	196.5	19506.8	(410.5)	19917.3
$^3D_2$			(54.2) 19452.6	(411.7)	(53.0) 19864.3
$^3D_3$					(87.2) 19777.1

The wave numbers are given for each line, as well as both the horizontal and vertical differences. Thus 19310.3 is the wave-number for the line $^3P_0 - {}^3D_1$, and the difference in wave number for this line and the line $^3P_1 - {}^3D_1$ is 196.5. For lines terminating on the same D level, the values of $\Delta \tilde{\nu}$ should be in the ratio 1 : 2 according to the rule, while the actually observed values are 196.5 and 410.5. For lines terminating on the same P level, the values of $\Delta \tilde{\nu}$ according to the rule are in the ratio 2 : 3, while the observed values are 53.0 and 87.2.

It follows that for the four levels $^4F_{3/2}$, $^4F_{5/2}$, $^4F_{7/2}$ and $^4F_{9/2}$ the values of $\Delta \tilde{\nu}$ for the separations $^4F_{5/2} - {}^4F_{3/2}$, $^4F_{7/2} - {}^4F_{5/2}$ and $^4F_{9/2} - {}^4F_{7/2}$ should be in the ratio 5 : 7 : 9, and in the case of the ^5D term, for which the values of J

[1] Hund, Linienspektren, p. 80.

are 0, 1, 2, 3 and 4, the values of $\Delta\bar{\nu}$ for the successive components should be in the ratio $1 : 2 : 3 : 4$.

The validity of Landé's rule has been demonstrated in a large number of cases, and as mentioned already, it has been possible, by application of the rule, to determine in the case of complex spectra, the proper assignment of J-values.

Finally, we shall mention briefly the extension of the same type of argument to jj-coupling, which is illustrated in Fig. 15.8 *B*. In this type of coupling, the spin-spin interaction is considerably less than for LS-coupling, but not negligible. For the four Γ-factors mentioned above, the following relations are deduced:

$$\Gamma_1 + \Gamma_2 = \frac{A}{2}\left\{J(J+1) - j_1(j_1+1) - j_2(j_2+1)\right\},$$

$$\Gamma_3 = \frac{a_3}{2}\left\{j_1(j_1+1) - l_1(l_1+1) - s_1(s_1+1)\right\},$$

$$\Gamma_4 = \frac{a_4}{2}\left\{j_2(j_2+1) - l_2(l_2+1) - s_2(s_2+1)\right\}.$$

As in the case of Pauli's g-permanence rule for the splitting up of terms in magnetic fields (mentioned in Section 12(2)) we have Landé's Γ-*permanence rule.* "This rule may be stated as follows: *For a given multiple term, i.e., given S and L, or given j_1 and j_2, the sum of all the Γ factors for terms with the same magnetic quantum number M is a constant independent of the field strength.*" [1]

Also in analogy with Pauli's g-sum rule, S. Goudsmit [2] has proposed the Γ-*sum rule* which is as follows: "*For a given electron configuration the sum of the Γ values corresponding to a given value of M is independent of the field strength H.*"

16. INTENSITIES OF SPECTRAL LINES

(1) **Quantum Mechanics Calculation of Intensities and Selection Principles:** [3] In classical electromagnetic theory the source of radiation is assumed to be an electron oscillating about a unit positive charge at a fixed point, in accordance with the relation

$$x = x_0 \cos 2\pi\nu t,$$

where x_0 = maximum amplitude, and ν = frequency of radiation emitted. Such an electric oscillator (which is often designated a *dipole*) will have a variable moment, M, defined by the relation

$$M = ex = ex_0 \cos 2\pi\nu t. \tag{16.1}$$

According to the electromagnetic theory radiation occurs when a charge is

[1] Ref. H. E. W., pp. 242–4.

[2] *Phys. Rev.*, 31, 946 (1928); also ref. P. G., pp. 157–165.

[3] The discussion in this section is based upon the remarks by S. D., *op. cit.*, Chap. XV.

accelerated, and the rate of emission of energy is then given by the relation

$$-\frac{dE}{dt} = \frac{2e^3}{3c^3}\left(\frac{d^2x}{dt^2}\right)^2, \qquad (16.2)$$

where x is the coordinate along which the motion occurs.

From equations (16.1) and (16.2) it follows that for the linear harmonic oscillator,

$$-\frac{dE}{dt} = \frac{2(2\pi\nu)^4}{3c^3} e^2 x_0^2 \cos^2 (2\pi\nu t).$$

Hence, the average rate of emission of energy per oscillator is

$$S = -\left(\overline{\frac{dE}{dt}}\right) = (2\pi\nu)^4 \frac{e^2 x_0^2}{3c^3}, \qquad (16.3)$$

since the average value of $\cos^2 (2\pi\nu t)$ is $\frac{1}{2}$. It will be noted that the *frequency of the radiation is identical* with *that of the oscillator.*

If the charge, instead of being concentrated at a point, is represented by a distribution function $\rho(x, y, z)$ as in the case of a negative charge distribution about a positive charge at the origin, the electric moment of the system will be represented by a *vector*

$$\mathbf{M} = e\int \mathbf{r}\, \rho(x, y, z) dx dy dz \cdot \cos (2\pi\nu t), \qquad (16.4)$$

where $\mathbf{r}$ is the *vectorial distance* measured from the origin. Denoting the components of $\mathbf{M}$ along the three axes of coordinates by $\mathbf{M}_x$, $\mathbf{M}_y$ and $\mathbf{M}_z$, the intensity of the radiation for which the direction of polarization is along the x-axis is given by

$$S_x = \frac{(2\pi\nu)^4}{3c^3} \cdot \overline{\mathbf{M}_x^2}, \qquad (16.5)$$

and similar relations will apply to the components $\mathbf{M}_y$ and $\mathbf{M}_z$ and the corresponding directions of polarization for the radiation emitted. Consequently, the average rate of emission of radiation per atom for all three components is given by

$$S_x + S_y + S_z = \frac{(2\pi\nu)^4}{3c^3} \left\{\overline{\mathbf{M}_x^2} + \overline{\mathbf{M}_y^2} + \overline{\mathbf{M}_z^2}\right\}$$

$$= \frac{(2\pi\nu)^4}{3c^3} \cdot \overline{\mathbf{M}^2}, \qquad (16.6)$$

where the bars designate time-average values of the squares.

Now the Bohr theory of the origin of spectral lines represented a radical departure from the classical point of view inasmuch as it postulated the relation

$$\nu_{mn} = \frac{E_m - E_n}{h},$$

where ν_{mn} is the frequency emitted as a result of a transition from state m to state n. How may we apply the results obtained with the classical model of a harmonic oscillator as a source of radiation, to the emission of radiation as a result of quantum transitions?

Bohr obtained a solution by means of the Correspondence Principle. As pointed out previously, this principle states that for orbits of very large quantum number, the frequency of radiation emitted is an integral multiple of the frequency of revolution of the electron. Consequently it is possible to calculate the value of a component, such as S_x, of the radiation emitted, by calculating the average value of $\overline{M_x^2}$ for the orbit.

In the case of a charge moving in some form of periodic orbit, the motion along any coordinate q ($q = x$, y, *or* z) can be represented by a Fourrier series of the form,

$$q = A_0 + A_1 \cos 2\pi\nu t + \cdots + A_n \cos 2\pi n\nu t + \cdots$$
$$B_1 \sin 2\pi\nu t + \cdots + B_n \sin 2\pi n\nu t + \cdots \qquad (16.7)$$

where A_n and B_n are the so-called Fourier coefficients for the harmonic of frequency $n\nu$. It may be shown that for such a motion, the time average value of q^2 is given by the relation,

$$\overline{q^2} = \sum_n (A_n^2 + B_n^2), \qquad (16.8)$$

and consequently,

$$S = \frac{(2\pi\nu)^4 c^2 \overline{q^2}}{3c^3}$$
$$= \frac{(2\pi\nu)^4 e^2}{3c^3} \sum_n (A_n^2 + B_n^2), \qquad (16.9)$$

where S represents the intensity of radiation for which the direction of polarization is along the direction of the coordinate q.

If now, in any given case, $A_n = B_n = 0$, this leads to the conclusion that the harmonic of frequency $n\nu$ cannot occur in the radiation emitted. Thus, in the case of a circular orbit, the only frequency associated with the motion of the electron is the fundamental, corresponding to $n = 1$. Hence, for such an orbit, the only possible transitions are those for which $\Delta n = \pm 1$. In this manner Bohr was able to deduce the Selection Principles for quantum numbers which have been stated in previous sections.

With the formulation of the new quantum mechanics and its model of a charge distribution function, which takes the place of the Bohr orbit, it became necessary to translate the classical results in terms of the new ideas. In quantum mechanics the complete eigenfunction for a given state is represented by the product of the form

$$\psi_n = \phi_n e^{-2\pi i (E_n/h) t},$$

where E_n is the eigenvalue associated with the eigenfunction ϕ_n, which is a

function of the coordinates. The product of the function ψ_n by its complex conjugate, $\bar{\psi}_n$, leads to the distribution function $\bar{\psi}_n\psi_n = \bar{\phi}_n\phi_n$ (in which the exponential factors cancel out), which is independent of time and is interpreted, as mentioned previously, in the following manner. If, for instance, ϕ_n is a function of x, y, z, then $\bar{\phi}_n\phi_n dxdydz$ corresponds to the probability of occurrence of the particle in the element $dxdydz$ at the point designated by the coordinates x, y, z. Instead of regarding $\bar{\phi}_n\phi_n$ as a probability distribution function, it is more convenient usually to consider it as a *charge density distribution* function.

Now let us consider the product

$$\mathbf{M}_x{}^{mn} = e \int x\psi_m\bar{\psi}_n d\tau + e \int x\psi_n\bar{\psi}_m d\tau,$$

where $d\tau$ = element of volume. This may evidently be written in the form

$$\mathbf{M}_x{}^{mn} = e \int x\phi_m\bar{\phi}_n e^{-2\pi i\nu_{nm}t}d\tau + e \int x\bar{\phi}_m\phi_n e^{2\pi i\nu_{nm}t}d\tau. \qquad (16.10)$$

Noting that

$$e^{-i\alpha x} = \cos \alpha x - i \sin \alpha x,$$

it is seen that $\mathbf{M}_x{}^{nm}$ is a harmonic function of the time in which the frequencies are identical with those given by the Bohr frequency relation for a transition between states for which the energy values are E_m and E_n.

Equation (16.10) thus resembles equation (16.4) for the variable moment of a charge distribution. Only in the quantum mechanics case the sum of the two integrals takes the place of the single integral in the latter. We have thus introduced a *fictitious* moment, which represents the moment due to the transition from state m to state n.

A rigorous calculation shows that the intensity of dipole radiation for which the direction of polarization is along the x-coordinate is given by

$$S_x{}^{mn} = \left[\frac{d^2\mathbf{M}_x{}^{mn}}{dt^2} \right]^2$$

$$= \frac{(2\pi\nu_{mn})^4 4e^2}{3c^3} x_{mn}x_{nm}, \qquad (16.11)$$

where

$$x_{mn} = \int x\phi_m\bar{\phi}_n d\tau \left.\vphantom{\int}\right\}$$

and

$$x_{nm} = \int x\phi_n\bar{\phi}_m d\tau \qquad (16.12)$$

The total rate of emission of energy per atom is therefore given by

$$S^{mn} = \frac{64\pi^4\nu^4{}_{nm}e^2}{3c^3} \{x_{mn}x_{nm} + y_{mn}y_{nm} + z_{mn}z_{nm}\}, \qquad (16.13)$$

where y_{mn} represents an integral similar to that in equation (16.12) with y replacing x, and similarly for the other integrals.

By the application of equation (16.11) or (16.13), it is thus possible to calculate the intensity of polarized or unpolarized radiation emitted for any given case. As in the classical quantum calculations, if one or more of the products $x_{mn}x_{nm}$ in these equations is found to vanish, this leads to a selection principle governing the occurrence of the corresponding transitions. It is thus possible from a knowledge of the eigenfunctions to deduce not only the selection principles mentioned in previous sections, but also in special cases the intensities of spectral lines.[1]

Incidentally, it should be observed that the integrals x_{nm}, etc., are known as *matrix elements*, since it is possible, for different values of n and m, to arrange these integrals in the form of a square array or matrix in which n designates the order in a row, and m the order in a column. Evidently the elements x_{nn} will occur along the diagonal of the matrix, while elements x_{nm} and x_{mn} will occur in positions which are symmetrical with respect to the diagonal.

On the basis of equation (16.13) it is possible to obtain an explanation of Laporte's rule, mentioned in the discussion of anomalous terms. According to this rule, which applies to simultaneous transitions of two electrons, such transitions are possible only from even terms (those for which $\sum l$ is even) to odd terms or *vice versa*.

Now for an electron configuration consisting of more than one electron in the valence shell, the total eigenfunction is approximately equal to the product of the eigenfunctions for the single electrons. An application of this rule has been made in a previous section in the discussion of the eigenfunction for the helium atom. It follows that the total eigenfunction is even or odd, according as $\sum l$ is even or odd. In mathematics a function $f(x, y, z)$ is said to be even, if $f(+x, +y, +z) = f(-x, -y, -z)$, and odd if it changes sign when the signs of the coordinates are changed.

From equation (16.13) it is evident that the intensity of dipole radiation emitted because of a transition between two states of the system will depend upon the magnitude of matrix elements similar to x_{mn}. The integrand in this integral is evidently an odd function if ϕ_m and $\bar{\phi}_n$ are either both even or both odd; since in either case it will change sign when $+x$ is changed to $-x$, and hence the integral (which is taken over all values of x from $+\infty$ to $-\infty$) will vanish. But if ϕ_n is even and ϕ_m odd, or vice versa, the integrand will be an even function and consequently the integrand will differ from zero.

By calculating the magnitudes of the matrix elements for different types of transitions, selection rules have been deduced for dipole radiation, which, although they have been stated previously in different sections, may be summarized as follows: [2]

[1] See ref. C. S. for comprehensive discussion of this topic, especially with regard to intensities of atomic hydrogen lines.

[2] Ref. H. E. W., p. 204.

For transitions involving only a single electron, $\Delta l = 0$; for transitions involving two electrons, $\Delta l_1 = \pm 1$, and $\Delta l_2 = 0$ or ± 2.

For the different types of spectral terms arising from all possible electron configurations, we may have either LS-coupling or jj-coupling.

For LS-coupling, the restrictions are:

$$\left.\begin{array}{l} \Delta S = 0, \\ \Delta L = 0, \quad \text{or} \quad \pm 1, \\ \Delta J = 0, \quad \text{or} \quad \pm 1, \end{array}\right\} \tag{16.14}$$

and in addition, the transition $J = 0$ to $J = 0$ is excluded.

For jj-coupling, the restrictions are:

$$\left.\begin{array}{l} \Delta j_1 = 0, \\ \Delta j_2 = 0, \quad \pm 1 \end{array}\right\} \text{or vice versa,} \left.\begin{array}{l} \\ \\ \end{array}\right\} \tag{16.15}$$
$$\Delta J = 0, \quad \text{or} \quad \pm 1,$$

and as before, the transition $J = 0$ to $J = 0$ is excluded.

As will be pointed out in the discussion of so-called forbidden lines, transitions are observed under certain conditions which apparently violate these selection rules. However, these may usually be explained (see subsequent section) as arising from variable quadrupole or variable magnetic dipole moments.

(2) **The Einstein Transition Probabilities:** [1] In Einstein's derivation of the Planck equation for black body radiation [2] three coefficients were introduced which are of importance in the consideration of spectral intensities. Let us consider two quantum states m and n of a system such that the energy level E_m is higher than E_n. Transition from the upper to the lower state is accompanied by emission of radiation of frequency

$$\nu_{mn} = \frac{E_m - E_n}{h} .$$

We shall assume that we have a large number of identical systems (atoms or molecules) in equilibrium with black body radiation at a temperature T. Then the rate at which systems pass spontaneously from state m to n, by emission of radiation, is given by

$$-\left(\frac{dN_m}{dt}\right)_1 = A_m^n N_m, \tag{16.16}$$

where A_m^n is known as *Einstein's coefficient of spontaneous emission*, and N_m is the number of systems in state m. But the rate at which systems can pass from the upper to lower state is also dependent upon the density of the radia-

---

[1] The discussion in this section follows closely that of ref. P. G., Chap. VIII. See also ref. P. W., p. 299 *et seq.*

[2] See Section 6(7).

tion, $\rho(\nu_{mn})$, so that we have a second process defined by the relation,

$$-\left(\frac{dN_m}{dt}\right)_2 = B_m^n N_m \rho(\nu_{mn}), \qquad (16.17)$$

where B_m^n is known as *Einstein's coefficient of induced emission.*

Furthermore, the system can pass from the lower to the upper state by absorption of radiation, and the rate of this reaction will be given by

$$-\frac{dN_n}{dt} = B_n^m N_n \rho(\nu_{mn}), \qquad (16.18)$$

where N_n = number of systems in quantum state n, and B_n^m is known as *Einstein's coefficient of absorption.*

At equilibrium,

$$\left(\frac{dN_m}{dt}\right)_1 + \left(\frac{dN_m}{dt}\right)_2 = \frac{dN_n}{dt};$$

hence,

$$B_n^m \rho(\nu)\frac{N_n}{N_m} = A_m^n + B_m^n \rho(\nu). \qquad (16.19)*$$

According to the Boltzmann relation,

$$\frac{N_n}{N_m} = \frac{g_n}{g_m} e^{-(E_n - E_m)/kT} = \frac{g_n}{g_m} e^{h\nu/kT}, \qquad (16.20)$$

where g_n and g_m are the so-called *a priori probabilities* or *statistical weights.* Substituting from the last equation in (16.19), the result is

$$\rho(\nu) = \frac{A_m^n}{B_n^m(g_n/g_m)e^{h\nu/kT} - B_m^n}. \qquad (16.21)$$

But according to Planck's law,

$$\rho(\nu) = \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{h\nu/kT} - 1}. \qquad (16.22)$$

Hence,

$$B_m^n = \frac{g_n}{g_m} B_n^m \qquad (16.23)$$

and

$$A_m^n = \frac{8\pi h\nu^3}{c^3} B_m^n. \qquad (16.24)$$

* In this and subsequent equations $\nu = \nu_{mn}$.

Now the energy radiated per unit time per atom in state m is given by

$$S^{mn} = A^n_m h \nu_{mn}. \qquad (16.25)$$

Comparing this with equation (16.13), it follows that

$$A^n_m = \frac{64\pi^4 \nu^3_{mn} M^2}{3hc^3}, \qquad (16.26)$$

where $M^2 = e^2(x_{nm}x_{mn} + y_{nm}y_{mn} + z_{nm}z_{mn})$.

Thus the transition probabilities for spectral lines might be calculated in the same manner as the intensities, from the eigenfunctions for the associated energy states. However, in view of the difficulties involved in applying equation (16.25) to any but the simplest cases, values of the transition probabilities have been derived from two kinds of observations: first, from measurements of the intensities of spectral lines, and by application of equation (16.25); second, from observations on the dispersion of light in gases and vapors. These methods will be discussed in a subsequent section.

(3) **Intensities of Spectral Lines:** It was noticed by spectroscopists that for the two D lines of sodium, i.e., the lines $^2S_{1/2} - {}^2P_{1/2}(\lambda 5890)$, and $^2S_{1/2} - {}^2P_{3/2}(\lambda 5896)$, the intensities of the two components are in the ratio $1 : 2$ respectively. A similar relation has been observed for other doublets in the same series and for analogous doublets in the spectra of the other alkali metals. That is, the relative intensities are independent of n, the total quantum number, but depend only upon the values of L and J for the two levels between which the transition occurs.

For triplets in the alkaline earth series and in the spectra of Zn and Cd, it has also been observed that the intensities of the three components $^3S_1 - {}^3P_0$, $^3S_1 - {}^3P_1$, and $^3S_1 - {}^3P_2$ are in the ratio $1 : 3 : 5$ respectively.

From these observations Burger, Dorgelo and Ornstein [1] deduced quantitative rules for the relative intensities of spectral lines which have been deduced subsequently by the application of quantum mechanics. These rules are as follows: [2]

"(1) The *sum of the intensities* of all lines of a multiplet which start from a common initial level is proportional to the quantum weight $(2J + 1)$ of the initial level.

(2) The *sum of the intensities* of all lines of a multiplet which end on a common final level is proportional to the quantum weight $(2J + 1)$ of the final level."

It will be recognized that $2J + 1$ is the number of levels into which a level of quantum number J is split by a magnetic field.

Let us consider the application of these rules to doublets of the types $^2S_{1/2} - {}^2P_{1/2, \, 3/2}$ and $^2P_{1/2, \, 3/2} - {}^2D_{3/2, \, 5/2}$. For the first one we immediately

[1] H. C. Burger and H. B. Dorgelo, *Z. Physik*, **23**, 258 (1924); L. S. Ornstein and H. C. Burger, *ibid.*, **22**, 170 (1924); **24**, 41 (1924).

[2] Ref. H. E. W., p. 205.

deduce the result:

$$\frac{{}^2S_{1/2} - {}^2P_{1/2}}{{}^2S_{1/2} - {}^2P_{3/2}} = \frac{2(\frac{1}{2}) + 1}{2(\frac{3}{2}) + 1} = \frac{2}{4},$$

which is in agreement with the observation.

For the other type, the possible transitions may be shown most conveniently by arranging the levels as in Table 16.1.

TABLE 16.1

	${}^2P_{3/2}(4)$	${}^2P_{1/2}(2)$	
${}^2D_{5/2}(6)$	$a = 9$	0	9
${}^2D_{3/2}(4)$	$b = 1$	$c = 5$	6
	10	5	

The numbers in brackets give the values of $2J + 1$, and the letters a, b, c are the relative intensities. The transition ${}^2P_{1/2} - {}^2D_{5/2}$ is forbidden and is therefore indicated by 0. Applying the "sum rule" we obtain the following equations:

$$\frac{a + b}{4} = \frac{c}{2}; \qquad \frac{b + c}{4} = \frac{a}{6}$$

the solution of which is $a = 9b, c = 5b$, as shown in Table 16.1. The numbers in the last column and those in the bottom row illustrate the application of the sum rule.

For multiplets of higher order, the number of available equations is less than the number of ratios. However, by application of the Correspondence Principle a number of investigators succeeded in deriving relations for the calculation of relative intensities in these more complex cases,[1] and these deductions have been confirmed by quantum mechanics calculations.

As an illustration of the application of these formulae and of the sum rule, Table 16.2 gives relative intensities for the components of the triplet ${}^3P_{0, 1, 2} - {}^3D_{1, 2, 3}$. The numbers in brackets give the values of $2J + 1$, and it will be seen that the values of Σ are those deduced from the sum rule.

TABLE 16.2

	${}^3P_0(1)$	${}^3P_1(3)$	${}^3P_2(5)$	Σ
${}^3D_1(3)$	20	15	1	36
${}^3D_2(5)$	—	45	15	60
${}^3D_3(7)$	—	—	84	84
Σ	20	60	100	

[1] Ref. H. E. W., pp. 205–7; see also ref. A. C. C., Vol. 2, Chap. XVII.

For multiplets of higher degree, as well as for multiplets in the Zeeman effect, tables are available,[1] based upon the equations mentioned above, for calculating the relative intensities of the components.

(4) **" Life " of Excited Atoms:**[2] Integrating equation (16.16) we obtain the equation

$$(N_m)_t = (N_m)_0 e^{-A_m^n t}, \tag{16.27}$$

which gives the relation between the number of atoms in quantum state m at $t = t$ and the number at $t = 0$. This is the equation of a first order reaction, and evidently

$$\tau = 1/A_m^n \tag{16.28a}$$

defines the so-called *"mean life"* of the atom in state m, that is, the period in which the number of atoms decreases to $1/e$th of its original value. Equation (16.27) is of course valid if the transition $m \rightarrow n$ is the only one that can occur. In general, the excited atoms can return to lower states in several ways. In that case,

$$\tau = \frac{1}{\sum\limits_{n} A_m^n}, \tag{16.28b}$$

where the summation is taken over all the states corresponding to different values of n, to which spontaneous transition can occur from the upper state m.

Before proceeding to discuss some of the methods which have been used for the determination of τ for various spectral lines, it is essential to point out that a similar magnitude was deduced from classical electromagnetic theory. For a charge oscillating about a point in accordance with the law of a linear harmonic oscillator, the "damping-period," τ_0, is given by the relation

$$\tau_0 = \frac{3mc^3}{8\pi^2 e^2 \nu_0^2}, \tag{16.29a}$$

where ν_0 is the frequency of the oscillator (and hence, the frequency of radiation emitted or absorbed) and e is the electronic charge. In terms of the wave length, λ_0, this expression becomes

$$\tau_0 = \frac{3mc}{8\pi^2 e^2} \lambda_0^2 = 4.50 \times 10^{-16} \lambda_0^2, \tag{16.29b}$$

where λ_0 is expressed in Å units. Thus for $\lambda = 5000$Å, $\tau_0 = 1.125 \times 10^{-8}$ sec. In view of the fact that quantum mechanics yields, in general, results which are at least of the same order of magnitude as classical theory, it would therefore be expected that for spectral lines, τ and A_m^n would be of the order of 10^{-8} sec., and 10^8 sec.$^{-1}$ respectively.

[1] Ref. A. C. C., and ref. C. S., Chap. IX.

[2] For comprehensive discussion of this topic see Resonance Radiation and Excited Atoms, by A. C. G. Mitchell and M. W. Zemansky, The Macmillan Company, New York, (1934). (Ref. M. Z.).

The most direct method for the determination of τ depends upon the measurement of the intensity of the spectral line. For a gas in *thermal* equilibrium at temperature T, the ratio between concentrations of atoms in the upper and lower states respectively is given by the Einstein-Boltzmann relation,

$$\frac{N_2}{N_1} = \frac{g_1}{g_2} e^{-E/kT}, \tag{16.20}$$

where 1 refers to the lower, 2 to the upper state, and E is the difference in energy between the two states. Applied to a resonance line, N_1 = concentration of atoms in normal states and N_2 = concentration of atoms in resonance state.

The total energy emitted per unit time per unit volume is

$$S = \frac{N_2 h \nu_{12}}{\tau} = \frac{N_1 h \nu}{\tau} \cdot \frac{g_1}{g_2} e^{-E/kT}. \tag{16.30}$$

Hence τ or $A(= 1/\tau)$ can be deduced from a measurement of S. As pointed out by R. Ladenburg,[1] the actually measured value of S has to be corrected for self-absorption of the radiation in the gas and the Doppler-effect broadening. From measurements of the intensities of the D-lines produced in a sodium flame, E. F. M. van der Held and L. S. Ornstein [2] obtained by application of the above equation the value $\tau = 1.63 \times 10^{-8}$ sec. for the 3^2P levels.

L. S. Ornstein and H. Brinkman [3] have pointed out that since the temperatures attained in arcs in air between carbon electrodes are quite high (5000° to 6000° K.), it is possible to obtain thermal excitation under these conditions of some of the elements for which E is comparable with kT in equation (16.20) or (16.30).

L. S. Ornstein, J. P. A. Hengstum and H. Brinkman [4] have used this method of excitation to deduce relative values of transition probabilities for some of the lines of cadmium. In this case, the relative transition probabilities are calculated from the relative intensities by means of the equation,

$$\frac{I_1}{I_2} = \frac{A_1 g_1 \nu_1 e^{-E_1/kT}}{A_2 g_2 \nu_2 e^{-E_2/kT}}, \tag{16.31}$$

where E_1 is the excitation energy of the level from which the line of frequency ν_1 emanates, g_1 is the statistical weight of the level and I_1 is the intensity of the line emitted, with similar notation for the other line of frequency ν_2. The lines investigated were those ending on the levels $5^3P_{2, 1, 0}$ and emanating from the next higher $^3S_1$ and $^3D_{3, 2, 1}$ levels.

The most accurate determinations of τ have been derived from absorption measurements. Let I be the intensity of a parallel beam of light transmitted

[1] *Rev. Mod. Phys.*, **5**, 243 (1933). S corresponds to H_{kj} in equation (6), p. 246 of this paper.

[2] *Z. Physik*, **77**, 459 (1932).

[3] *Proc. Amsterdam Acad.*, **34**, 33 (1931).

[4] *Physica*, **5**, 145 (1938).

through a cell containing a monatomic gas or vapor. In the neighborhood of the resonance line for the particular gas, absorption will occur in accordance with the relation,

$$I_\nu = I_0 e^{-k_\nu x}, \tag{16.32}$$

where x = thickness of absorption layer, I_0 = incident intensity, and I_ν = intensity of transmitted light of frequency ν. A plot of k_ν (which has the dimensions cm.$^{-1}$) versus ν will appear as in Fig. 16.1,[1] in which the maximum
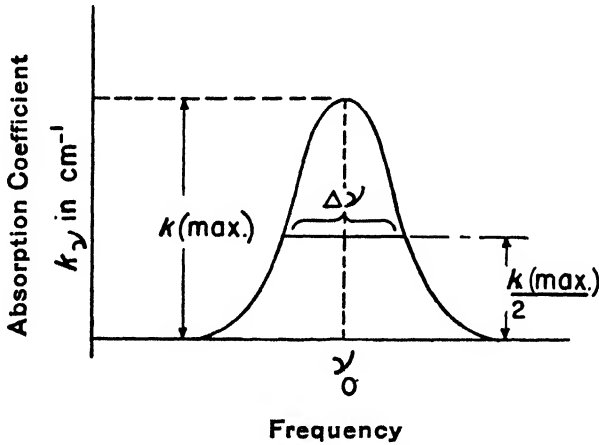

FIG. 16.1. Absorption Versus Frequency Near a Resonance Line

value of k_ν ($= k_{\max}$) occurs for $\nu = \nu_0$.

It can be shown that for relatively low concentrations of excited atoms ($N_2 < 10^{-4} N_1$ where N_1 = concentration of atoms in normal state, and N_2 = concentration in excited state),[2]

$$\int_0^\infty k_\nu d\nu = \text{area under curve}$$

$$= h\nu N_1 B_1^2/c$$

$$= \frac{h\nu N_1}{c} \cdot \frac{g_2}{g_1} \cdot \frac{c^3}{8\pi h \nu_0^3} A_2^1$$

$$= \frac{\lambda_0^2 g_2}{8\pi g_1} N_1 A_2^1, \tag{16.33}$$

where λ_0 = wave length of the pure resonance line.

[1] Ref. M. Z., p. 93.

[2] Tolman, Statistical Mechanics, 1st edition, Chapter 16. See also M. Z., *op. cit.*, p. 95.

On the other hand, the classical theory yields the relation

$$\int_0^\infty k_\nu d\nu = \frac{\pi e^2}{mc} N_1 f, \tag{16.34}$$

where f is known as the equivalent "oscillator strength" of the line. If the N_1 atoms per cc. behaved like a similar number of "quasi-elastically bound" electrons, the value of f would be unity. The ratio f thus represents the *number of classical oscillators per atom.* This ratio is found to be constant for any given spectral line. As Mitchell and Zemansky point out:[1] "The f-value associated with a spectral line emitted by an atom can be regarded as a measure of the degree to which the ability of the atom to absorb and emit this line resembles such an ability on the part of a classical oscillating electron. In all classical formulas of normal and anomalous dispersion, magnetorotation and absorption, the quantity f appears."

From equations (16.33) and (16.34) it follows that:

$$f_{21} = \frac{mc}{8\pi^2 e^2} \cdot \frac{g_2}{g_1} \lambda_{21}^2 A_2^1 \tag{16.35}$$

or

$$f_{21}\tau_2 = 1.50 \times 10^{-16}(g_2/g_1)\lambda_{21}^2, \tag{16.36}$$

where λ_{21} is expressed in Å units.

Equation (16.36) is strictly valid for the case in which there is only one transition from level 2 to level 1.

It also follows from equation (16.35) and equation (16.29b) that

$$f_{21} = \frac{\tau_0}{3\tau_2} \cdot \frac{g_2}{g_1}, \tag{16.37}$$

which indicates another interpretation of the ratio f.

The first experiments on the determination of τ were carried out by W. Wien.[2] By measuring the rate of decay of luminosity in the canal rays (positive ions) passing out behind the cathode of a discharge tube, he deduced the value $\tau = 2.3 \times 10^{-8}$ sec. in the case of the H_β and H_γ lines of hydrogen. Using a direct electrical method, F. G. Slack[3] has obtained the result $\tau = 1.2 \times 10^{-8}$.

While equation (16.33) may be used to yield a value for τ from absorption measurements, a more direct method has been used extensively which depends upon the application of equation (16.27). Assuming that excited atoms in the resonance state are produced only as a result of collisions between electrons and atoms and that the radiation comes from a very thin layer of the absorbing atoms, the intensity of radiation at any instant is a measure of the number of

[1] Ref. M. Z., p. 96. For a discussion of the significance of f from the point of view of the older quantum theory see R. Ladenburg and F. Reiche, *Naturwiss.*, 11, 584 (1923).

[2] *Ann. Physik*, 60, 597 (1919); 66, 229 (1921).

[3] *Phys. Rev.*, 28, 1 (1926).

excited atoms. Consequently the value of τ may be derived from observations on the intensity as a function of time after the production of excited atoms has ceased.

Since, according to equation (16.36) a determination of either τ or f yields a value for the other constant, we must also consider a method which has been used extensively for the determination of f-values. According to classical theory, the refractive index (r) for a gas in a region of frequencies which does not lie too near to any of the resonance frequencies, is given by the relation

$$r^2 = 1 + \frac{f}{\pi m} \cdot \frac{Ne^2}{(\nu_0{}^2 - \nu^2)}, \tag{16.38}$$

where $\qquad\qquad N = $ number of atoms per cc.,

and $\qquad\qquad \nu_0 = $ resonance frequency.

In this equation Nf corresponds to the number of so-called "dispersion electrons," and f represents again, the number of classical oscillators per atom. Since r is not very different from unity, equation (16.38) may also be written in the form,

$$r - 1 = \frac{f}{2\pi m} \cdot \frac{Ne^2}{(\nu_0{}^2 - \nu^2)} . \tag{16.39}$$

The quantum theory modification of this relation is given by

$$r - 1 = \frac{e^2}{2\pi m} \cdot \frac{F_{kj}}{(\nu_{kj}{}^2 - \nu^2)}, \tag{16.40}$$

where

$$F_{kj} = N_j f_{kj} \left(1 - \frac{N_k}{N_j} \cdot \frac{g_i}{g_k} \right). \tag{16.41}$$

In these equations, j is the *lower* and k the *upper* level of the spectral line of frequency ν_{kj} and N_j and N_k are the concentrations of atoms for these levels. The expression $N_k g_i / N_j g_k$ (designated by Q_{kj}) is a correction term which takes into account the "induced emission" postulated in Einstein's theory.[1] The correction is obviously appreciable only in those cases for which N_k is comparable with N_j. Neglecting this term, equation (16.41) assumes, for values of λ very close to that of $\lambda_0 = \lambda_{kj} = c/\nu_{kj}$, the form,

$$r - 1 = \frac{e^2 Nf}{4\pi mc^2} \cdot \frac{\lambda_0{}^3}{\lambda - \lambda_0}, \tag{16.42}$$

where $f = f_{kj}$ and $N = N_j$.

In the neighborhood of λ_0, the refractive index decreases with decrease in λ and this phenomenon is designated *anomalous dispersion*.[2]

The results of the measurements obtained by numerous investigators have

---

[1] See equation (16.17).

[2] For a discussion of optical dispersion and of equations (16.38) to (16.42) see the review by A. Korff and G. Breit, *Rev. Mod. Phys.*, **4**, 471 (1932).

TABLE 16.3

Element	Resonance Line	g_2/g_1	λ_0	$f\tau \times 10^9$	τ in secs.	f-value
Na......	$3^2S_{1/2} - 3^2P_{1/2}$	1	5896	5.21	1.48×10^{-8}	0.35
	$3^2S_{1/2} - 3^2P_{3/2}$	2	5890	10.42	1.48×10^{-8}	0.70
K.......	$4^2S_{1/2} - 4^2P_{1/2}$	1	7699	8.90	2.7×10^{-8}	0.33
	$4^2S_{1/2} - 4^2P_{3/2}$	2	7665	17.8	2.7×10^{-8}	0.67
Cs......	$6^2S_{1/2} - 6^2P_{1/2}$	1	8944	12.1	3.8×10^{-8}	0.32
	$6^2S_{1/2} - 6^2P_{3/2}$	2	8521	21.9	3.3×10^{-8}	0.66
Cd......	$5^1S_0 - 5^3P_1$	3	3261	4.77	2.5×10^{-6}	0.0019
	$5^1S_0 - 5^1P_1$	3	2288	2.35	1.98×10^{-9}	1.20
Hg......	$6^1S_0 - 6^3P_1$	3	2537	2.90	1.08×10^{-7}	0.0277
	$6^1S_0 - 6^1P_1$	3	1849	1.54	1.30×10^{-9}	1.19

been summarized by Mitchell and Zemansky [1] and some of the values which the latter consider the most reliable are given in Table 16.3.

More recently R. B. King and D. C. Stockbarger [2] have determined absolute values of f by the method of total absorption. The values obtained were $f = 0.0023$ for the Cd line $\lambda 3261$, and $f = 0.62$ and 0.32 for the Cu lines $\lambda 3427$ and $\lambda 3274$ respectively.

It is of interest to note that the values of τ for different lines vary from approximately 10^{-9} sec. to 10^{-6} sec. For transitions of the intercombination type $^1S_0 - {}^3P_1$ the values of τ are considerably higher than those for transitions of type $^1S_0 - {}^1P_1$. This is in accord with the theoretical deductions (mentioned previously) that in absence of spin-orbit interaction intercombination lines should not occur.

By applying a formula developed first by Pauli, on the basis of the Correspondence Principle, and confirmed by Houston on the basis of wave mechanics, it is possible to calculate the ratio τ_1/τ_3 where $\tau_1 = $ life of the lowest $^1P_1$ state of a two-electron atom, and $\tau_3 = $ life of the lowest $^3P_1$ state. Some of the values thus deduced, as tabulated by Mitchell and Zemansky, are given in Table 16.4 in the third column.

TABLE 16.4

Atom	ν_3/ν_1	τ_1/τ_3	(f_1/f_3) calc.	(f_1/f_3) obs.
Ca.......	0.643	1.25×10^{-5}	30,180	33,000
Zn.......	.695	6.71×10^{-5}	6,757	7,200
Sr.......	.668	2.69×10^{-4}	1,582	1,660
Cd......	.702	8.0×10^{-4}	637	680
Ba.......	.700	3.35×10^{-3}	169	146
Hg......	.728	1.2×10^{-2}	53.4	46.8

[1] Ref. M. Z., pp. 145–7. A similar table is given on p. 62 of Gasentladungstabellen, by M. Knoll, F. Ollendorf and R. Rompe, Julius Springer, Berlin(1935). This will be referred to as "Gas-Tabellen."

[2] *Astrophys. J.*, **91**, 488 (1940).

G. W. King and J. H. Van Vleck [1] have used a modified form of Houston's formula to calculate the relative f-values for these transitions. The values thus deduced as compared with observed values (according to King and Van Vleck) are given in the last two columns of the above table. The very high value of the ratio for Ca as compared with the considerably lower value for Hg is in agreement with the statement made above regarding the role of spin-orbit interaction.

It should be noted that in the case of Zn, W. Billiter [2] has reported for τ_1 and τ_3 the values 1.78×10^{-9} sec., and 2.64×10^{-5} sec., respectively, or a ratio τ_1/τ_3 of 6.74×10^{-5}, which is in good agreement with the value given above by Mitchell and Zemansky.

From equation (16.37) it follows that for values of $g_2/g_1 = 3$, $f = \tau_0/\tau$. It will be observed that for many of the transitions listed in Table 16.3, f is of the order of unity. That is, the radiation emitted is of the classical type.

So far the discussion has dealt mainly with the determination of τ for resonance states, for which N_j in equation (16.41) is identical with that of the atoms in the gas or vapor. If the system is in *thermal* equilibrium, then the concentrations of atoms excited to different states (N_k) may be calculated in terms of the concentration of atoms in a lower state (N_j) by the Boltzmann-Einstein relation,

$$\ln Q_{kj} = \ln N_k - \ln N_j - \ln (g_k/g_j)$$
$$= - (E_k - E_j)/kT, \tag{16.43}$$

of which equation (16.20) is a special case. In this equation, E_k and E_j refer to the energy values for the two states k and j.

However, in the positive column of an electric discharge in a gas or vapor at low pressure, the relative concentrations for different states of excitation are determined by such factors as the current, pressure, and dimensions of the discharge tube, and not by the temperature of the gas in the tube. Consequently the actual values of N_j for an excited state and the values of f and A for lines terminating on this level, have to be determined by other methods. Since these methods are specially applicable to so-called metastable atoms, they will be discussed in the following section.

In conclusion it should be observed that from the value of f or τ for a resonance line it is possible to deduce values of this constant for higher members of the same series by comparing the relative intensities of the lines. In this manner it has been found, and the observation is supported by quantum mechanics considerations, that the value of f is highest for the resonance line and decreases with increase in the values of the energy for the levels from which the lines emanate. Thus for the principal series in the spectrum of sodium, the values of f for the first ten lines (designated by the value of n) are shown in Table 16.5.[3]

[1] *Phys. Rev.*, **56**, 464 (1939).

[2] *Helv. Phys. Acta*, **7**, 505 (1934).

[3] A. Filipov and W. K. Prokofjew, *Z. Physik*, **56**, 458 (1929). This and similar tables for other elements are given in the review by Korff and Breit, *loc. cit.*

TABLE 16.5

n	λ	f	n	λ	f
1	5893	97.55	6	2544	0.0134
2	3303	1.40	7	2512	.0081
3	2853	0.205	8	2491	.0054
4	2680	.063	9	2476	.0038
5	2594	.026	10	2464	.0028

Similar observations have been made by D. Sinclair and H. W. Webb [1] on the values of τ for the doublet levels of K. For $\lambda 4044$-7 and $\lambda 3447$-6, the values of τ obtained were 3.79×10^{-7} sec., and 8.5×10^{-4} sec. respectively, which are greater than the values for the resonance doublet as given in Table 16.3.

TABLE 16.6

CRITICAL POTENTIALS, METASTABLE LEVELS AND RESONANCE LINES

Element	Excitation Energy in Volts				λ	λ	V_i
	$^3P_2{}^*$	$^3P_1$	$^3P_0{}^*$	$^1P_1$	$^1S_0 - {}^3P_1$	$^1S_0 - {}^1P_1$	
Ne	16.61	16.67	16.72	16.84	744	736	21.56
A	11.55	11.62	11.72	11.82	1067	1048	15.76
Kr	9.90	10.03	10.56	10.64	1236	1165	14.00
Xe	8.31	8.43	9.45	9.57	1469	1295	12.13
	$^3P_0{}^*$	$^3P_1$	$^3P_2{}^*$	$^1P_1$			
Zn	4.01	4.03	4.08	5.79	3076	2139	9.39
Cd	3.73	3.80	3.88	5.42	3261	2288	8.99
Hg	4.67	4.89	5.46	6.70	2537	1849	10.43
	$^3S_0{}^*$	$^1S_0{}^*$	$^3P_{0,1,2}$	$^1P_1$		$^1S_0 - {}^1P_1$	
He	19.81	20.61	20.95	21.20		584	24.58

* Indicates metastable level.

(5) **Metastable States:** In the energy level diagram for mercury (Fig. 1.6) it is observed that no transition occurs between the $^3P_0$ or the $^3P_2$ level and the normal, $^1S_0$, level, as these transitions are forbidden by the selection principle for the inner quantum number J.

[1] *Phys. Rev.*, **50**, 397, 440 (1936).

Thus a mercury atom in the excited state $^3P_0$ or $^3P_2$ cannot give up its energy in the form of radiation but must ultimately return to the normal state by some other process. However, it has been deduced on the basis of wave mechanics that the value of the Einstein coefficient A_m^n for the transition from such a state as $^3P_0$ or $^3P_2$ is not zero, but merely extremely low.

Similar states are observed in the spectra of other atoms with two or more electrons in the outer shell, as for instance, those of Ca, Zn, He, Ne, A and also in the spectra of more complex atoms. They are known as *metastable* states and the investigations on the behavior of atomic systems in this state have yielded very interesting results.

For the purpose of ready reference in the subsequent discussion, Table 16.6 gives values of critical potentials, metastable levels and resonance lines for the rare gases and the vapors of Zn, Cd and Hg. The metastable levels are indicated in this table by an asterisk. Fig. 16.2 shows these lower levels for
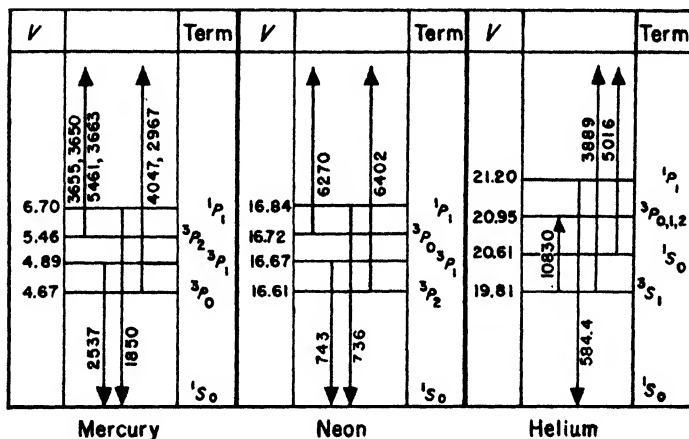
FIG. 16.2.   Lower Levels in the Spectra of Hg, Ne and He

Hg, Ne and He respectively, with absorption lines which end on metastable levels.[1]

There are four ways in which an excited atom, in the metastable state, may change from this state.

(1) It may receive a further increment of energy by collision with an electron, and thus be raised to a still higher energy state, as, for example, in the case of mercury, to the next higher $^3S_1$ or $^3D_1$ level, from which transitions are possible by emission of radiation. This process by which an atom is raised by collision with electrons from one excited state to higher states is known as *cumulative excitation*. In fact, it is possible for an atom in the meta-

[1] The values of the energy levels have been re-calculated from the corresponding wave numbers as given in ref. B. G., by means of the conversion factor 1 volt = 8067.7 cm.$^{-1}$.

stable state to receive sufficient energy by this process to be ionized, and this is designated as *cumulative ionization*.

(2) An atom in the metastable state may receive radiation of just the right frequency to be absorbed and thus be raised to one of the next higher levels. For instance, in the case of the metastable state $^3P_0$ in mercury, energy of wave length $\lambda 4047$ incident upon an electric discharge in mercury vapor (in which there will be a considerable concentration of metastable atoms) will be absorbed and destroy some of the metastable atoms by exciting them to the $^3S_1$ level. Indeed, observations on the absorption of light by metastable atoms in an electric discharge in neon or helium have been used for the determination of the mean life of metastable states in these gases.[1] These observations are discussed more fully in a subsequent section.

A similar phenomenon is also observed in the absorption of light by atoms excited to states which are not metastable. For instance, R. W. Wood and others [2] have carried out some very striking experiments with mercury vapor which illustrate the occurrence of this phenomenon. By exposing mercury vapor in a resonance tube to the light from two separate mercury arcs operated under different conditions, the mercury atoms were excited in succession by $\lambda 2537$ and then by $\lambda 3125$–3131 (see Fig. 1.6), thus causing the emission of the lines 2967, 3655 and 3663. These lines could not be produced if either source of light was used by itself.

On the basis of the quantum theory these observations are interpreted by the relations

$$E_1 + h\nu_{12} = E_2,$$
$$E_2 + h\nu_{23} = E_3,$$
$$E_3 - h\nu_{31} = E_1,$$

where ν_{12} and ν_{23} are frequencies of absorbed radiation and ν_{31} the frequency of emitted radiation.

Similarly, if mercury vapor is irradiated with light of wave lengths 2537 and 4358, emission is observed of the triplet lines 4047, 4358 and 5461, which as shown in Fig. 1.6 correspond to transitions from the 2^3S_1 state.

This process in which two radiation quanta are absorbed in succession is analogous to the process of *cumulative excitation* (mentioned above) by electron collisions. It also may be regarded as a qualitative indication that ordinary excited states have a finite life, even though the actual magnitude of this period is less than that of metastable atoms.

(3) The metastable state may be destroyed by collisions with other atoms in the normal state. (These are known as *collisions of the second kind* for reasons which will be given in a subsequent section.) According to the kinetic theory the average kinetic energy of a molecule is $\frac{3}{2}kT = 6.21 \times 10^{-14}$ erg at

---

[1] H. B. Dorgelo and T. P. K. Washington, *Roy. Acad. Sci. Amsterdam*, **35**, 1009 (1926); also K. W. Meissner and W. Graffunder, *Ann. Physik*, **84**, 1009 (1927).

[2] *Proc. Roy. Soc.*, [A], **106**, 679 (1924). See also E. Gaviola and R. W. Wood, *Phil. Mag.*, **6**, 1154, 1167, 1191 (1928).

$T = 300°$ K.   This corresponds to $6.21 \times 10^{-14}/1.602 \times 10^{-16} = 3.88 \times 10^{-2}$ electron volt.   Hence there will be a considerable fraction of the molecules with energies between about 0.02 and 0.08 electron volts.   If the difference between the energy value for a metastable state and that for the nearest excited state is of the order of 0.05 volts, there may be an interchange of energy between the normal and metastable atoms in such a direction as to convert the latter into an excited state from which transitions are not forbidden.

(4) If there is present an admixed gas, B, whose atoms have an ionization energy lower than the excitation voltage of the metastable state for the atoms of the gas A, then a collision between a metastable atom A and an atom of B may result in ionization of the latter, and a return of the metastable atom to its normal state.   This phenomenon is of special importance in electrical discharges in mixed gases.

For instance in argon at a pressure of a few mm. in which is present mercury vapor at a pressure of about 10^{-3} mm., metastable argon atoms produced in the discharge (energy 11.55 and 11.72 volts) readily transfer this energy to mercury atoms with resultant production of ions (for which $V_i = 10.43$ volts).

The problem of the mean life of metastable atoms, which we shall designate by τ_m, has been the subject of a number of investigations.   The principal gases in which such metastable states have been studied are the members of the rare gas group and mercury.[1]

Meissner and Graffunder [2] have reviewed the different experimental methods for the determination of τ_m and have devised a method of their own which they consider as most reliable.   This method may be described by referring to the energy diagram for mercury, Fig. 1.6.   A discharge is passed through the vapor for a while, and then cut off.   After a definite interval of time, the absorption of the mercury is measured for the line $\lambda 4047$ ending on the 2^3P_0 level or the line $\lambda 5461$ ending on 2^3P_2.   The absorption decreases exponentially with time and it is assumed that the intensity of absorption is proportional to the number of atoms in the metastable state.   From the observed rate of decay it is thus possible to calculate τ_m which is the time required for the number of metastable atoms to decrease to $1/e$th of their original value.   As shown by Meissner and Graffunder and by M. Zemansky,[3] who has also carefully considered the theory of this method, the actual observations must be corrected for diffusion of metastable atoms to the walls and for collisions of the second kind.

According to Asada, Ladenburg and Tietze,[4] the life of the $^3P_0$ state for mercury under most favorable conditions is $\tau_m = 15 \times 10^{-4}$ sec.   The persistence of radiation $\lambda 2537$ observed by Webb and Messenger [5] is explained by Zemansky [6] on the basis of this result as due to collisions between metastable

[1] For detailed discussion see ref. M. Z., pp. 236–257 and list of references to 1933.

[2] *Loc. cit.*

[3] *Phys. Rev.*, **34**, 213 (1929).

[4] *Physik. Z.*, **29**, 549 (1928).

[5] *Phys. Rev.*, **33**, 319 (1929).

[6] *Loc. cit.*

$^3P_0$ atoms with excited mercury atoms, by which the former are raised to the $^3P_1$ state, from which the line λ2537 is produced.

The lower energy states for *neon* are shown in the diagram Fig. 16.3. The two resonance lines λ744 and λ736 correspond to transitions from the $^3P_1$ and
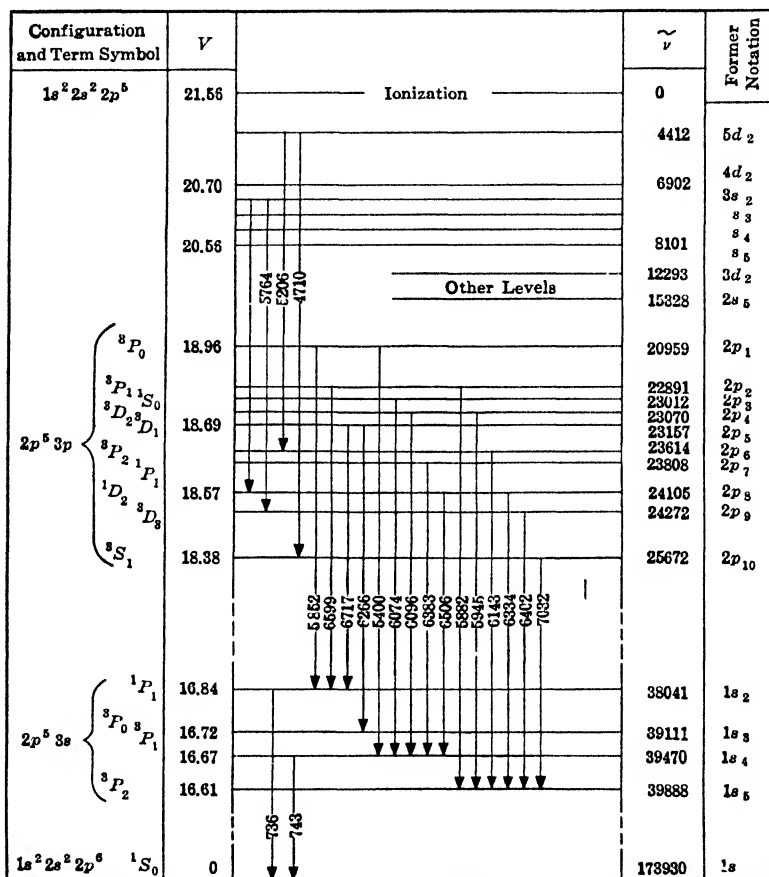
FIG. 16.3.   Energy Level Diagram for Neon

$^1P_1$ states respectively. The $^3P_2$ and $^3P_0$ levels represent metastable states, and it will be observed that the lines λ6402 and λ6143 correspond to resonance lines for one of these states. As shown by a careful examination of the spectrum of neon in the far ultra-violet [1] no transitions are observed from the $^3P_2$ or $^3P_0$ states to the normal ($^1S_0$) level. On the other hand, as shown by Meissner and W. Graffunder [2] the lines λ6402 and λ6143 are absorbed by neon when excited

[1] H. B. Dorgelo and Abbink, *Z. Physik*, **37**, 667 (1926).

[2] *Ann. Physik*, **76**, 124 (1925); **84**, 1009 (1927).

by an electric discharge. By measuring the absorption of the excited neon for these two lines as a function of the time after excitation they deduced for the $^3P_2$ state a value of τ_m which varied for different pressures of neon from about 1.64×10^{-4} to 3.57×10^{-4} sec. According to their results, the variation with pressure can be represented by a relation of the form

$$\frac{1}{\tau_m} = \frac{B}{p} + Cp, \qquad (16.44)$$

where p = pressure, and B and C are empirical constants.

In the case of helium, as shown in Fig. 16.2 the lowest metastable state requires 19.81 volts for excitation. Using the method devised by Meissner and Graffunder, "E. Ebbinghaus [1] measured the absorption of the helium line $\lambda 10830$ by excited helium as a function of time after the cut-off of the excitation." From Fig. 16.2 it is evident that the magnitude of the absorption is a measure of the concentration of 2^3S_1 atoms. The observed value of τ_m for a pressure of helium of 3.0 mm. Hg was 1.67×10^{-3} sec.

The energy levels for argon are similar to those for neon, and there exist two corresponding metastable states. (See Table 16.6.) For the lowest metastable state, J. M. Anderson,[2] using the absorption method, obtained for $p = 0.22$ mm., the values $\tau_m = 1.23 \times 10^{-3}$ at 300° K, and $\tau_m = 10 \times 10^{-3}$ at 80° K.

In both helium and argon, the variation of τ_m with pressure is in agreement with equation (16.44) and M. Zemansky has shown that this relation as well as the observed increase in τ_m with decrease in temperature are most satisfactorily interpreted on the assumption that metastable atoms lose energy by diffusion to the walls and by collision with gas molecules.

The rate of diffusion to the walls varies inversely as the pressure and this accounts for the first term in equation (16.44), (B/p), while the rate at which metastable atoms collied with normal atoms varies directly as the pressure, and this gives rise to the term Cp.

Measurements by E. W. Pike [3] on the life of metastable neon atoms gave the following numerical results: at 36 mm. pressure, τ for $^3P_2$ state $= 2 \times 10^{-3}/p$, sec. and for the $^3P_1$ resonance state, $\tau = 4 \times 10^{-5}/p$, sec. where p = pressure in mm. of mercury. From these observations Pike deduces a value for the coefficient of diffusion of excited neon atoms which is of the same order of magnitude as the kinetic theory value for neon atoms.

Metastable states are of special significance in the interpretation of observations on the light emission from the positive column of an electric discharge in mercury vapor or in any of the rare gases, or in mixtures of these gases and the vapor of a metal such as mercury or sodium. Indeed, most of our knowledge of metastable states and of excited states in general has been obtained from

[1] *Ann. Physik*, **7**, 267 (1930); ref. M. Z., p. 245.

[2] *Canad. J. Res.*, **4**, 312 (1931).

[3] *Phys. Rev.*, **49**, 513 (1936).

investigations carried out by means of arcs or other forms of electrical discharges in gases or vapors. The only other process (outside of chemical reactions) by which light is emitted is that of thermal excitation and ionization, of which cosmic light sources provide the most important examples. In these cases, however, the temperatures attained vary from 5000° K for relatively cold stars to values which are many times greater for the hotter stars.[1]

By means of equation (16.43) it is possible to calculate the relative concentrations of atoms for different states of excitation as a function of T. Expressing the energy in electron volts and using ordinary logarithms, this equation assumes the form [2]

$$\log Q_{kj} = \log (N_k/N_j) - \log (g_k/g_j)$$
$$= -5040(V_k - V_j)/T. \qquad (16.45)$$

Table 16.7 gives values of n/N, for a series of temperatures for the lowest resonance states in Cs and Hg. For Cs, the lowest state is $^2P_{1/2}(V = 1.386,\ g_k/g_j = 1)$, and for Hg, the corresponding state is $^3P_1(V = 4.89,\ g_k/g_j = 3)$.

TABLE 16.7

| | CORRESPONDING VALUE OF T | |
n/N	For $^2P_{1/2}$ state in Cs	For $^3P_1$ state in Hg
10^{-4}	1750	6,930
10^{-3}	2330	8,920
10^{-2}	3490	12,500
10^{-1}	6980	21,000

It will be observed that except in the case of cesium, the degree of excitation is extremely low at any value of T attainable in the laboratory.[3]

It is largely for this reason that positive column discharges have been used to provide most of our information regarding the life and concentrations of excited states. Because of the impossibility of applying equation (16.43) to such discharges, for which the temperature of the gas is usually 300° K to 500° K, it is necessary to supplement the observations on anomalous dispersion (which as is evident from equation (16.41) yield only values of F_{kj}) by other observations in order to obtain N_j, f and A for individual excited states.

The procedure devised by R. Ladenburg and his collaborators during the course of a series of investigations on metastable and higher excited states in the rare gases and mercury, has been described by Ladenburg [4] as follows: [5]

---

[1] These values refer, of course, to surface temperatures. The internal temperatures are most probably of the order of millions of degrees Kelvin.

[2] $V = T(k/e) = T/11,604$ volts and $11,604/2.3026 = 5040$.

[3] This remark applies to temperatures attainable by means of furnaces, and not to exceptionally high temperatures such as have been obtained by exploding wires.

[4] *Rev. Mod. Phys.*, 5, 243 (1933). This gives an excellent review of the work of the author and of others, over a number of years, on "Dispersion in Electrically Excited Gases."

[5] This method is applicable only when the quantity Q_{kj} as defined in equation (16.43) is small compared to unity.

"Light from a source giving a continuous spectrum—a black body or a carbon arc or an incandescent lamp—is passed through the luminous gas and analyzed by a spectrograph of high dispersion. The resulting spectrum will show the spectral lines of the gas either as dark or as bright lines depending on whether the black-body temperature of the source is above or below a critical temperature T_r, called the *reversal temperature*, at which the lines just disappear against the continuous background. If there is statistical equilibrium for the different excited states in the gas corresponding to a common temperature, all lines reverse at the same temperature, but in general they do not. Each line has its own characteristic reversal temperature. The length of path, the strength of absorption and the resolution of the spectrograph influence the accuracy of the setting, but not the value of T_r. The only assumption is, that the luminous gas layer passed by the rays of the light source is uniform and that the ratio N_k/N_j of the population of the two states belonging to the line investigated has a definite value along the light path. This ratio or rather the ratio Q of Eq. (16.41) is given, as Hedwig Kohn has shown,[1] by an equation identical in form with Boltzmann's equation

$$Q_{kj} = e^{-(E_k - E_j)/kT_r}, \tag{16.46}$$

because the disappearance of the line against the continuous background means that every volume of the gas absorbs as much radiation energy as it emits." That is, equation (16.43) or (16.45) is applicable, with T_r replacing T.

The measurements on anomalous dispersion give, as equation (16.41) shows, the values of $F_{kj} = N_j f_{kj}$. On the other hand, the so-called "true intensity" for a spectral line is given, in accordance with equation (16.30) by the relation

$$H_{kj} = N_k A_{kj} h\nu_{kj}. \tag{16.47}$$

"If we compare," Ladenburg continues, "two lines with the same upper level (let us say a) and with different lower levels (say b and c) we get from the intensity ratio of these lines the ratio of their A values and from measurements of their anomalous dispersion the ratio of their F values, and thus we get the ratio $N_b : N_c$)."

The absolute values of f may be estimated by applying the "f-sum rule" of Thomas-Reiche-Kuhn:

$$\sum_a f_a - \sum_e f_e = Z, \tag{16.48a}$$

where Z designates in this case the number of "effective" electrons per atom. The first sum refers to all possible *absorption* transitions of the atom in the state considered and the second sum to all *emission* transitions of this state. For a metastable state $\sum f_e = 0$. Hence,

$$\sum_k N_j f_{jk} = \sum_k F_{jk} = A N_j. \tag{16.48b}$$

[1] H. Kohn, *Physik. Z.*, **29**, 49 (1928); **33**, 957 (1932).

For neon Z is between 1 and 2 (since only one, or at the most, two electrons take part in absorption), and consequently the values of f for the different lines may be determined within certain limits. In this manner values of f and A have been obtained for different lines ending on the lowest metastable level ($^3P_2$ state) for neon, and values of τ for the upper levels (p_1p_2 to p_{10} in the older notation) from which they emanate. The values obtained range from 0.8×10^{-8} to 2×10^{-8} sec. for the different levels.

From the same measurements of F_{kj} and H_{kj} it is possible to calculate the relative concentrations in the different excited levels. In this manner it was found that for a discharge in neon the concentrations in the different levels increase with the current I, in accordance with a relation of the form

$$N_j = \frac{\alpha I}{1 + \beta I}, \tag{16.49}$$

where α and β are constants. This equation indicates that at larger currents, the excited atoms are destroyed by collisions with electrons, so that ultimately "a kind of statistical equilibrium is attained between colliding electrons and excited atoms."

Figure 16.4 [1] shows the variation in concentration of metastable neon atoms as a function of current.
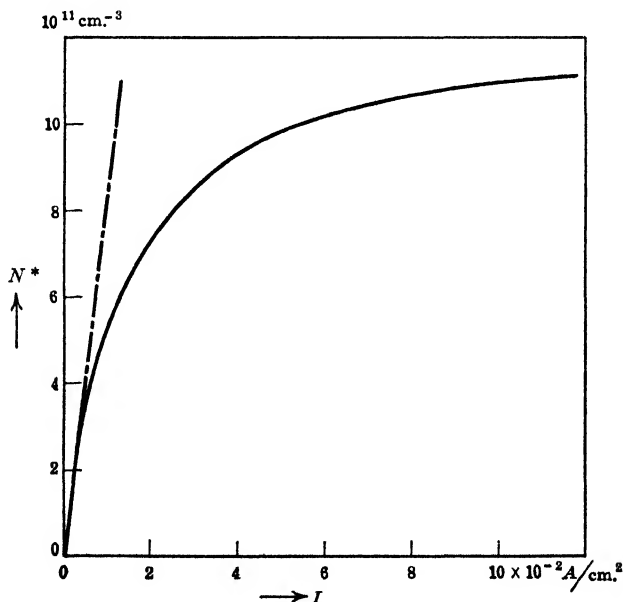
FIG. 16.4.   Variation with Current of Concentration of Metastable Atoms
in Electrical Discharge in Neon

[1] A. v. Engel and M. Steenbeck, Elektrische Gasentladungen, p. 140, Julius Springer, Berlin (1932).

Under these conditions it was found that the relative concentrations of atoms in the different levels could be represented by the modified Boltzmann relation, equation (16.45), in which T corresponds to the *"electron temperature"*. In the positive column of a discharge, which constitutes the so-called "plasma," [1] the electrons attain a Maxwellian distribution of velocities which corresponds to that for a gas at a temperature T_e.

Ladenburg found for discharges in neon at a pressure of 1 mm. of Hg, and with currents ranging up to 300 m.a. a value of T_r from the measurements on temperature of reversal, of about 22,000° K, which agreed well with the value for T_e of about 20,200° K obtained by means of the probe method.[2]

Letting N_m designate the concentration of atoms in the metastable $^3P_2$ state ($V = 16.61$, $g = 5$) and N that in the normal state ($g = 1$) the value of N_m/N as deduced by means of equation (16.45) for $T = 20,000°$ K is 3.24×10^{-4}. Since the approximate value of N at 1 mm. and $T = 300°$ is 3.2×10^{15}, $N_m \sim 1 \times 10^{11}$, which is in good agreement with results obtained by other investigators. For the five p levels from which transitions are observed to the $^3P_2$ level, the values of N_p/N_m obtained at the highest currents ranged around 0.38 (where N_p is the concentration in the p-level).

It should be mentioned that in this investigation it was observed that with large increase in current, beyond 300 m.a., a decrease in the value of F_{kj} was observed, and this was interpreted as due to the effect of "induced emission", that is, the term Q_{kj} in equation (16.41) could no longer be neglected.

Similar results have been obtained by other investigators. Thus W. Fabrikant, F. Butaewa and I. Zirg [3] have determined for a discharge in mercury vapor, at pressures ranging from 10^{-4} to 10^{-2} mm., the concentrations of excited atoms in the levels 6^3P_0, 6^3P_1 and 6^3P_2. Of these three levels 6^3P_1 is the resonance state for $\lambda 2537$ Å, while the other two represent metastable states. Table 16.8 gives the concentrations in the three states for a constant current of 3 amperes in a 3.2 cm. diameter tube, and for different pressures of mercury.

The theoretical values are those calculated in accordance with equation (16.45) assuming $T = T_e$. Evidently the experimental values of n could be accounted for by assuming a somewhat higher value for T. It is of interest to note that for the two extreme cases the values of N, the concentration of mercury atoms per cc., and the values of the ratio n/N are as follows:

p	Corresp. T	N	n	n/N
7.5×10^{-3}	316° K	2.3×10^{14}	13.8×10^{11}	0.006
2.5×10^{-4}	276° K	8.8×10^{12}	1.2×10^{11}	0.014

[1] For a discussion of the meaning of the terms, "plasma" and "electron temperature" and the phenomena in the positive column, see K. T. Compton and I. Langmuir, *Rev. Mod. Phys.*, **2**, 123 (1930); also K. K. Darrow, Electrical Phenomena in Gases, The Williams and Wilkins Company, Baltimore (1932). A brief survey of this field is given by S. Dushman, *J. Opt. Soc. Am.*, **27**, 1 (1937), which contains a copious list of references.

[2] See previous references for a description of this method.

[3] *Physik. Z. Sowjetunion*, **11**, 576 (1937).

TABLE 16.8

| p in mm. of Hg | $n \times 10^{-11}$ | | | | | |
| | 6^3P_0 | | 6^3P_1 | | 6^3P_2 | |
	exper.	theor.	exper.	theor.	exper.	theor.
2.5×10^{-4}	1.2	12	0.3	33	2.1	45
9.0×10^{-4}	2.5	29	0.96	76	7.2	103
2.9×10^{-3}	4.3	45	1.6	113	10.8	143
7.5×10^{-3}	4.9	54	4.5	123	13.8	143

The values of T are those corresponding to the vapor pressures given in the first column.

Thus the concentration of atoms in metastable states in these experiments was found to be about 1 per cent of that of atoms in the normal state.

From these measurements it was deduced that Einstein's coefficient $.1$ for the line $\lambda 2537$ ($^3P_1 \rightarrow {}^3S_0$) is 1.1×10^6 sec.$^{-1}$ which is in good agreement with observed value of $\tau = 0.9 \times 10^{-6}$ for the $^3P_1$ state. For the two metastable states the value $\tau_m = 0.7 \times 10^{-5}$ sec. was derived.

F. L. Mohler [1] has used the determination of the reversal temperature (T_r) to derive values for the concentration of atoms in different states of excitation in a positive column discharge in cesium vapor. Simultaneous measurements were made, by means of probes, on the electron temperature. The concentration in the resonance states ($2^2P_{1,2}$) was found to increase with both current and pressure, attaining a maximum value, in terms of atoms/cc., of about 10^{11}. The approximate agreement between the values of T_e and T_r showed that the values of the concentrations in the different levels are in substantial accord with those deduced from equation (16.45). For the n^3P_2 series of levels in mercury, it was observed that the concentration decreased with increase in n from 6×10^{12} for $n = 6$ (the lowest ^3P level) to 2.5×10^7 for $n = 11$.[2]

These observations thus lead to the conclusion that the relative concentrations of atoms in excited and normal levels for a positive column discharge in a gas at low pressures are those deduced from the Boltzmann equation with $T = T_e$. At higher pressures and larger current densities the whole character of a discharge changes radically.

Thus in a capillary mercury vapor lamp, the pressure varies from a few atmospheres at moderate current density to over 100 atmospheres in the water-cooled type. Accompanying this increase in both current density and pressure it is observed that the value of T_e approaches more and more closely that of the vapor in the center of the discharge, so that it is possible to apply to this case the Einstein-Boltzmann relation for thermal equilibrium.

[1] *J. Res. Nat. Bur. Stand.*, **9**, 493 (1932).
[2] *Ibid.*, **16**, 227 (1936).

(6) **Forbidden Lines:** In accordance with the selection principles certain transitions are forbidden. However, under special conditions some of these so-called forbidden lines become quite prominent and it is, therefore, of interest to enquire into some of the reasons for the occurrence of such lines.

A very important exception of this nature is the occurrence of intercombination lines such as $\lambda 2537$ ($2^3P_1 - 1^1S_0$) in the spectrum of mercury, while the corresponding intercombination line is not observed in the spectrum of helium, and is very faint in the spectrum of beryllium. As mentioned previously the presence of such lines violates the selection rule $\Delta S = 0$. However, this is valid only for pure Russell-Saunders coupling, and with increase in atomic number, spin-orbit interaction becomes more effective, so that the coupling is no longer that assumed by Russell-Saunders.

As pointed out in Section 16(1), the selection principles have been deduced by recognizing an analogy between the behavior of a classical electric dipole and the emission of radiation as the result of quantum transitions. Classically, however, radiation may also be emitted by a *quadrupole*. If two dipoles are arranged linearly so that the two unit positive charges coincide and are located at the center of two unit negative charges separated by a distance $2x$, then $\sum e_i x_i = 0$, where x is the distance from the center. But such an arrangement of charges has a *quadrupole moment* of magnitude $\sum e_i x_i^2$, which is not equal to zero, since x_i^2 does not change sign in passing through the origin. While the potential energy due to a single charge at the origin varies as $1/r$ where r is the distance from the origin, that due to a dipole varies as $1/r^2$, while the potential energy due to a quadrupole varies as $1/r^3$, where r is large compared to the distance $2x$.

A variable quadrupole moment acts as a source of radiation, like a variable dipole moment, and in quantum mechanics the quadrupole radiation depends upon the magnitude of the matrix element $e \, | \int x^2 \bar{\psi}_n \psi_m d\tau \, |^2$. Because of the difference between this expression and the matrix element, $e \, | \int x \bar{\psi}_n \psi_m d\tau \, |^2$ involved in dipole radiation, the same selection rules are no longer applicable. Consequently transitions which are forbidden in the case of the latter, are no longer forbidden for quadrupole radiation. However, the transition probabilities (corresponding to $A_m{}^n$) are extremely small compared to those for dipole radiation, the ratio being about $10^{-8} : 1$.[1]

Forbidden transitions may also occur as a result of a variable *magnetic dipole moment*, for which the analogue is the electromagnetic radiation obtained from a coil carrying high frequency alternating current. If the two magnetic moments due to the vectors L and S do not compensate each other, a variable magnetic dipole moment results which may act as a source of radiation.

Finally forbidden lines may occur because of strong electric fields either applied externally or produced by neighboring atoms or ions (*enforced dipole radiation*).

In the case of metastable states the intrinsic probability of transition on the basis of quantum mechanics is not zero but extremely low, that is τ_m is of the

[1] Ref. G. H., p. 54, also pp. 154-6.

order of seconds.   Therefore in an ordinary light source, the metastable atom loses energy in a much shorter period either by collisions with other atoms (collisions of the second kind) or with electrons, or with the walls of the enclosure.   By decreasing the pressure the value of τ_m may be increased, as shown in the previous section, but it is not possible in practice to decrease the pressure to such a low value and increase the dimensions to such an extent that τ_m can be reduced to the theoretical value.   However, in stellar atmospheres the conditions are ideal in this respect, and it would therefore be expected that in these light sources forbidden transitions might be observed.

For a long time certain lines had been observed in cosmic nebulae, which could not be identified with any terrestrial light source.   Consequently these were ascribed to a non-existent element, *nebulium*.   However, I. S. Bowen first showed [1] that these lines are due to forbidden transitions between terms in the spectra of O_{II}, O_{III} and N_{II}.   For instance the two most prominent nebulium lines, N_1 and N_2 are due to the transitions $^3P_2 - {}^1D_2$ and $^3P_1 - {}^1D_2$ respectively in the spectrum of O_{III} (O^{++}), while another line corresponds to the transition $^4S_{3/2} - {}^2D_{3/2}$ in the spectrum of $O_{II}(O^+)$.

The green and red auroral lines have been obtained in the laboratory by J. C. McLennan and G. M. Shrum [2] and have been shown to correspond to the transitions $^1D - {}^1S$ and $^3P_{1,2} - {}^1D$, respectively, of the neutral O atom.   According to R. Frerichs and J. S. Campbell [3] these transitions are of the quadrupole type, while according to E. U. Condon [4] the nebulium lines N_1 and N_2 are due to magnetic dipole radiation.

As shown by the latter it is possible, on the assumption that forbidden lines are due to either magnetic dipole radiation or quadrupole radiation or to both causes, to calculate transition probabilities for these lines from the evaluation of the corresponding matrix elements.   More recently a series of calculations of this nature have been carried out by S. Pasternak [5] for a number of cases which are of importance in the spectra of nebullae and novae.

That forbidden transitions are prevalent in the spectra of a large number of atoms in the normal and stripped states is evident from the review of this topic by I. S. Bowen,[6] to which the reader is referred for a more comprehensive discussion.

(7) **Collisions of the Second Kind:** [7] Franck and Hertz demonstrated in 1913 that electrons, to which has been imparted a kinetic energy, Ve, by acceleration through a potential field, are able to transfer this energy, if it is of

[1] *Rev. Mod. Phys.*, **8**, 55 (1936).

[2] *Proc. Roy. Soc.*, [A], **108**, 501 (1925).

[3] *Phys. Rev.*, **36**, 151, 1460 (1930).

[4] *Astrophys. J.*, **79**, 217 (1934).

[5] *Astrophys. J.*, **92**, 129 (1940).

[6] *Loc. cit.*

[7] In connection with this topic the following treatises are of importance: (1) J. Franck and P. Jordan, Anregung von Quantensprüngen durch Stösse, Julius Springer, Berlin (1926); (2) Ref. M. Z.: (3) E. J. B. Willey, Collisions of the Second Kind, Edward Arnold & Co., London (1937).   (Ref. E. J. B. W.).

just the right amount, to an atom or molecule and thus excite or even ionize it. If excited, the atom will then give up its energy, after an interval τ, in the form of monochromatic radiation of frequency

$$h\nu \leqslant Ve.$$

Such a process which can be written symbolically in the form

atom + fast electron → excited atom + slow electron,
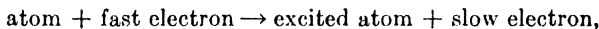
is known as a *collision of the first kind*. The effectiveness of such a collision in producing excited state or ionization depends on the magnitudes of certain probability factors which will be discussed in the following section.

O. Klein and S. Rosseland first pointed out [1] that on the basis of thermodynamical considerations other processes must be expected by which the concentration of excited atoms is prevented from increasing indefinitely. These considerations have been stated by Mitchell and Zemansky as follows: [2]

"In order to preserve thermodynamic equilibrium in a mixture of atoms and electrons, it is necessary to assume that some kind of reverse process to the one explained above must occur in which fast electrons and unexcited atoms result. Not only must we assume that at equilibrium the overall rate of formation of fast electrons and unexcited atoms must be the same as the overall rate of formation of excited atoms and slow electrons, but we are forced to make the postulate that : 'The total number of molecules leaving a given quantum state in unit time shall equal the number arriving in that state in unit time, and also the number leaving by any one particular path shall be equal to the number arriving by the reverse path.' [3] The postulate which entails that each *microscopic* process occurring must be accompanied by an inverse process is called the Principle of Microscopic Reversibility."

Klein and Rosseland, therefore concluded that if fast electrons can collide with unexcited atoms and produce excited atoms and slow electrons, then the reverse process must occur, that is, excited atoms should collide with slow electrons and produce unexcited atoms and fast electrons. Such a radiationless process has been designated a *collision of the second kind*, and evidently this process is exactly the reverse of that which occurs in a collision of the first kind.

The reasoning used by Klein and Rosseland may be described as follows: [4] Let us consider an enclosure at temperature T in which atoms in two states, represented by k (the upper level) and j (the lower level) are in equilibrium with electrons. Let E_k and E_j denote the energy values, and let $E_0 = E_k - E_j$, where E_0 is a positive quantity. According to Maxwell's law of distribution of

[1] *Z. Physik*, **4**, 46 (1921).

[2] Ref. M. Z., p. 57.

[3] See R. C. Tolman, *Proc. Nat. Acad. Sci.*, **11**, 436 (1925), where the above statement and a discussion of the Principle of Microscopic Reversibility are to be found.

[4] These remarks are based on the presentation by R. Ladenburg, *Rev. Mod. Phys.*, **5**, 251 (1933).

velocities, the number of electrons which have an energy between E and $E + dE$ is given by the relation

$$F(E)dE = Ce^{-E/kT}\sqrt{E}\,dE, \tag{16.50}$$

where C is a constant.   In order to excite atoms from the lower to the upper state, the electrons must have an energy $E_2 > E_0$.   Let $S_{jk}(E_2)$ designate the probability that such a collision of the first kind will result in excitation.   Then the number of collisions per unit time per unit volume which will result in excitation from the j to the k level is given by

$$N_1 = n_j F(E_2)S_{jk}(E_2),$$

where n_j = concentration of atoms in state j.

The energy of the electrons after the exciting collision is $E_1 = E_2 - E_0$. In a collision of the second kind these electrons may acquire the energy E_0 from excited atoms in state k, and if we let $S_{kj}(E_1)$ denote the probability of such a transfer of energy at a collision, then the frequency of such collisions per unit volume is given by

$$N_2 = n_k F(E_1)S_{kj}(E_1).$$

For equilibrium $N_1 = N_2$, and introducing Boltzmann's relation for the ratio n_k/n_j, equation (16.20), it follows that

$$g_j E_2^{1/2}S_{jk}(E_2) = g_k E_1^{1/2}S_{kj}(E_1). \tag{16.51}$$

Since $E_1 = E_2 - E_0$, and it is known that the probability of excitation increases very rapidly with increase in $E_2 - E_0$ (see following section), it follows that for values of $E_1 > 0$, $S_{kj}(E_1)$, which is the probability of occurrence of a collision of the second kind, must be appreciable.

The validity of this theory has been amply confirmed by subsequent investigations, such as those of H. Koppermann and R. Ladenburg [1] and of F. L. Mohler.[2]   J. Franck [3] extended the ideas of Klein and Rosseland to include collisions between excited and normal atoms or molecules.   "Thus he supposed that an excited atom might collide with a normal atom or molecule and give up a quantum of energy to the unexcited atom; the latter might then take up the energy either as translational energy, excitational energy, or both, there being no loss of energy by radiation during the process.   Such radiationless transfers of energy Franck also called collisions of the second kind." [4]

The destruction of metastable states by collisions of this type has been mentioned previously.   Such collisions also play an important role in modifying the light output from electrical discharges in such mixtures as $Hg + A$, or $Na + Ne$, both of which are of practical importance as light sources.   The

[1] *Z. Physik,* **48**, 15, 26, 51, 192 (1928); **65**, 167 (1930).

[2] *J. Res. Nat. Bur. Stand.,* **9**, 493 (1932).

[3] *Z. Physik,* **9**, 259 (1922).

[4] Ref. M. Z., p. 59.

so-called "quenching" of resonance radiation of mercury or sodium is another illustration of the effect of collisions of the second kind. If the light from a quartz mercury arc is arranged to strike an evacuated quartz bulb containing a drop of mercury the resonance line (λ2537) is absorbed by the mercury vapor so that little or no radiation passes through the vapor *directly*. However, the bulb now acts as a source of radiation of the pure resonance line owing to excitation of normal atoms by the absorbed radiation, and subsequent spontaneous emission of this radiation occurs in all directions (scattered radiation).[1] Such a source has been designated a *resonance lamp*. If the radiation from this source is now allowed to fall on another bulb containing mercury in a vacuum the same processes of absorption and re-emission of λ2637 are observed again. But if a gas such as nitrogen, water vapor, or hydrogen is introduced at low pressure into the second bulb, the intensity of the emitted radiation is decreased. It is said to have been "quenched."

Such experiments first performed with mercury resonance radiation by R. W. Wood in 1912, later by G. Cario,[2] and H. Stuart[3] and duplicated with resonance radiation from sodium and cadmium by Stuart and other investigators, are interpreted as due to destruction of excited atoms, before they are able to emit radiation, by collisions with molecules of the foreign gas.[4]

A much more important illustration of collisions of the second kind is furnished by the experiments on sensitized fluorescence and sensitized chemical reactions.

The former can occur under the following conditions. Consider a mixture of two gases A and B in which the resonance energy E_A is higher than the corresponding energy for the other gas, E_B. If now radiation of frequency $\nu_A = E_A/h$ is allowed to fall on the mixed gases, the atoms of A will become excited to the resonance state. If the number of atoms of B is so large that the time between collisions of atoms, A, with atoms, B, is comparable with or less than the mean life, τ, of the excited state of A, then, by collisions of the second kind, the energy E_A will be transferred to some of the atoms of B, since E_B is less than E_A. That is, atoms of B will be excited to the resonance state, and as a result radiation of frequency $\nu_B = E_B/h$ will be emitted. The excess energy, $E_A - E_B$, will appear as increased kinetic energy of the atoms B. We may describe the effect as a fluorescence of atoms B sensitized by the admixed atoms A. As in all fluorescence effects the frequency of the emitted radiation (ν_B) should be less than that of the incident radiation (Stokes's law).

The occurrence of this effect was first demonstrated by some experiments carried out by G. Cario[5] and also by Cario and Franck[6] on mixtures of mercury and thallium vapors. The resonance state for mercury (corresponding to

---

[1] This arrangement thus resembles that shown in Fig. 5.1 for the Raman effect.

[2] *Z. Physik*, **10**, 185 (1922).

[3] *Ibid.*, **32**, 262 (1925).

[4] The theory of this effect is discussed by M. Z., *op. cit.*, p. 191, *et seq.*

[5] *Z. Physik*, **10**, 185 (1922).

[6] *Ibid.*, **11**, 161 (1922).

emission of λ2537) requires 4.89 volts for excitation, whereas there are a number of states for thallium which are lower than this with respect to the ground state. As a consequence, a mixture of the two vapors emits, under excitation by λ2537, a number of lines in the spectrum of thallium for which the upper levels are below 4.89 volts.

In these and other experiments carried out with mixtures of cadmium and mercury vapors, lines were observed for which the upper levels are above 4.89 volts (anti-Stokes lines), and this has been interpreted as the result of a co-operation between the excitation energy and translational energy of the mercury atoms due to thermal motion.

H. Kallmann and F. London [1] have discussed this phenomenon from the point of view of quantum mechanics. For relatively low values of $\Delta E = E_A - E_B$ the values of the frequencies ν_A and ν_B are not very different. Consequently we should obtain, under these conditions, a *resonance effect*, similar to that which has been observed for two identical pendulums and which has also been found to occur between the two electrons in a helium atom. There results in such cases an interaction energy owing to the periodic transfer of energy from one system to the other with a frequency $\nu_A - \nu_B$. On the basis of considerations, similar in many respects to those involved in the calculation of the exchange or resonance energy for an excited helium atom (see Section 15(2)), Kallmann and London have shown that the interaction energy, $E_{AB}(R)$ (to indicate that it is a function of the interatomic distance, R), should be given (for small values of R) by the approximate relation

$$E_{AB}(R) \sim \mu_A \mu_B / R^3, \tag{16.52}$$

where μ_A and μ_B are the dipole moments of two virtual oscillators corresponding to the frequencies ν_A and ν_B respectively. The magnitudes of these moments may be deduced, on the basis of wave mechanics, from the wave functions for the two states associated with the energy values E_A and E_B.

During a collision the two atoms will approach within a minimum distance R_0 and the probability for the transfer of energy from atom A to B or vice versa will depend upon the relative values of the quantities $E_{AB}(R_0)$ and ΔE. If the ratio

$$\beta = \frac{2E_{AB}(R_0)}{\Delta E} \tag{16.53}$$

is very small, then the probability of energy transfer is practically zero. But as ΔE is decreased to values comparable with $E_{AB}(R_0)$, the magnitude of this probability increases. This effect may be described as an increase in the *effective cross section*, q, for collision, in excess of that deduced from simple kinetic theory considerations. As shown by Kallmann and London,

$$q = 0.960\pi(\mu_A\mu_B/\Delta E)^{2/3}. \tag{16.54}$$

[1] *Z. physik. Chem.* [**B**], **2**, 207 (1929).

Since the order of magnitude of μ_A or μ_B is approximately that of $ea_0/2$, where a_0 = radius of normal Bohr orbit, equation (16.54) may be expressed in the form

$$q = 0.38 \left(\frac{e^2}{a_0} \cdot \frac{1}{\Delta E} \right)^{2/3} \pi a_0^2, \qquad (16.55)$$

where πa_0 is evidently equal to the kinetic theory cross-section for collisions between hydrogen atoms. For $\Delta E \sim e^2/(2a_0) = 13.6$ volts, q evidently has approximately the same value as that deduced from kinetic theory considerations. That is, the probability of energy interchange between the atoms is zero. However, as the value of ΔE decreases and approaches that of $E_{AB}(R_0)$, the consequent increase in the probability of interchange of energy is indicated by a corresponding increase in the value of q. Thus for $\Delta E = 200$ cm.$^{-1}$ ($= 25 \times 10^{-3}$ electron-volt), q is 40 times that of the kinetic theory cross-section and *increases with decrease in* ΔE as shown in Fig. 16.5, which is taken
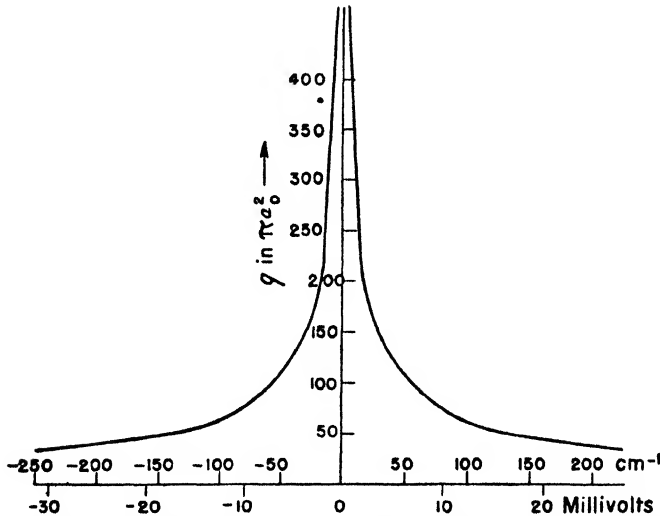
FIG. 16.5. "Effective Cross-Section" for Two States for Which the Energy Difference has the Value of ΔE. The plot shows q as a function of ΔE

from the original paper. It follows that the nearer the two energy states A and B, the sharper the resonance.

As an illustration of the application of these conclusions the observations by H. Beutler and B. Josephy [1] may be cited, on the fluorescence of sodium vapor by excited mercury atoms. The relative energies of the two excited states for mercury and the sensitized states for sodium are shown in Table 16.9, arranged with the normal levels on the last line, and E_A (or E_B) gives the energy

[1] *Z. Physik*, **53**, 747 (1929).

TABLE 16.9

ILLUSTRATING ENERGY TRANSFER FROM EXCITED Hg ATOMS TO Na ATOMS

Mercury				Sodium			
Term	$\bar{\nu}$	E_A	Volts	Term	$\bar{\nu}$	E_B	$-\Delta E$
6^3P_1	44,769	39409	4.89	$9^2S_{1/2}$	1874	39575	20×10^{-3}
6^3P_0	46,536	37642	4.67	$7^2S_{1/2}$	3437	38012	50×10^{-3}
6^1S_0	84,178	0	0	$3^2S_{1/2}$	41449	0	

(expressed in wave numbers) above that of the normal level. The last column gives the energy difference between the excited and sensitized states, which are located on the same horizontal line. Thus the 6^3P_1 level lies about 20×10^{-3} volt below the 9^2S level, and the 6^3P_0 level, about 50×10^{-3} volt below the 7^2S level.[1] The intensities of lines emanating from these sodium levels were found to be considerably increased with respect to those of other lines when mercury was present with the sodium and the mixed vapors were irradiated by the mercury resonance line $\lambda 2537$.

The fact that nitrogen is more effective than many other gases in quenching resonance radiation has been interpreted by London and Kallmann thus: The energy difference $^3P_1 - {}^3P_0$ for Hg (2.18×10^{-3} volt) is in resonance with the combined vibration and rotational energies (258×10^{-3} volt) of a nitrogen molecule.

The resonance effect has also been used to explain the observed *enhancement* in a discharge, of spectral lines or bands of a vapor or gas, by the addition of another gas, such as mercury or one of the rare gases. For instance, certain bands in the diatomic gases CO, N_2 and O_2 may be increased in intensity by diluting them with helium or neon.[2]

Similar observations have been made by O. S. Duffendack and his associates on the enhancement of certain spark lines of metallic vapors in neon and helium arcs. Thus Duffendack and K. Thomson[3] examined the intensities of certain groups of lines, all derived from a common upper level, in Ag, Au, Al and Cu(a) in the normal arc with addition of Ne or He and (b) in the condensed spark in the absence of any rare gas. If we designate by ΔE the difference between the energy level of ionized neon and the nearest upper level of the excited metal atom, the enhancement is greater, in general, for the lowest values of ΔE.

[1] Kallmann and London designate these levels in terms of the older notation as 7^2S and 5^2S respectively.

[2] Ref. E. J. B. W., pp. 9–11.

[3] *Phys. Rev.*, **43**, 106 (1933).

J. H. Manley and Duffendack [1] have obtained similar results for the excitation of a number of lines in the spectrum of Mg_{II} in presence of neon. Because of collisions of the second kind between excited neon atoms and magnesium ions the concentration of higher terms in the spectrum of ionized magnesium is increased considerably.

Another prediction from quantum theory, made by E. Wigner, [2] states that in a collision of the second kind angular momentum of electron spin is conserved. That is, "of all possible transfers of energy *that* one will be most likely to occur in which *the total resultant spin*, considered for the two atoms together, remains unchanged." [3]

For instance, in the case of a collision of a krypton atom in the metastable $(^3P_2)$ state, for which $S = 1$, with a mercury atom in the normal (6^1S_0) state, for which $S = 0$, and therefore $\Sigma S = 1 + 0 = 1$, the result of a collision might be either,

$$Kr(^1S_0) + Hg(8^1D) \text{ for which } \Sigma S = 0, \ \Delta E = -0.033 \text{ volt}$$

or

$$Kr(^1S_0) + Hg(8^3D) \text{ for which } \Sigma S = 1, \ \Delta E = -0.038 \text{ volt.}$$

Wigner's theorem states that the last named type of energy transfer would be more probable, since the value of ΣS remains constant. By examining the relative intensities of lines starting from the ^1D and ^3D states of mercury in presence of pure helium and helium containing an admixture of krypton, H. Beutler and W. Eisenschimmel [4] have verified this theorem.

Excited atoms may also sensitize certain chemical reactions, as was first shown by Cario and Franck. [5] For instance, hydrogen, activated by excited mercury atoms, reacts with certain oxides (such as CuO or WO_3) at room temperature, whereas in pure hydrogen alone, no reactions occur. Since the dissociation energy of H_2 is 4.455 volts (102,700 cal./mole), it was assumed at first that the activation process consists essentially in a dissociation of H_2 into atoms. However, there seem to be valid objections against this interpretation and other mechanisms have been suggested. [6]

The reaction between hydrogen and oxygen in presence of excited mercury atoms has been studied by many investigators and similarly the reaction between hydrogen and carbon monoxide. Since such investigations have served to throw considerable light upon the mechanism of a number of chemical reactions, this topic pertains more logically to the field of photochemistry than to that of atomic structure. [7]

[1] *Phys. Rev.*, **47**, 56 (1935).
[2] *Gött. Nachr.*, 375 (1927).
[3] Ref. M. Z., pp. 69–70.
[4] *Z. physik. Chem.*, [**B**], **10**, 89 (1930).
[5] *Z. Physik*, **11**, 161 (1922) and subsequent papers.
[6] For review of these explanations see ref. M. Z., pp. 71–85.
[7] A comprehensive review is given by ref. E. J. B. W.

(8) Collisions of Electrons with Atoms: [1] According to equation (16.47) the intensity of a spectral line is given by a relation of the form

$$I = A_m{}^n N_m h\nu_{mn}, \qquad (16.56)$$

where N_m is the concentration of atoms in state m, and the frequency ν_{mn} is due to a transition from the *upper* state, m, to *lower* state, n. The excited atoms are generated, in general, by collision of electrons having adequate kinetic energy, with atoms in the normal or in an excited state lower than m. It is therefore of interest to inquire into the efficiency of the processes by which excited atoms and ions are produced by collisions of the first kind.

Such collisions are divided into two classes, *elastic* and *inelastic*. If the electron has an energy, E, less than that corresponding to the lowest excited state of the atom, the collision is of the elastic type, and the electron loses only the very small amount of energy, $2mE/M$, where m and M denote the masses of electron and atom respectively. In an inelastic collision the electron loses that amount of its energy which corresponds to a transition between two quantum states of the atomic system.

However, even if the electron has sufficient energy to produce an excited state or ion, there is no certainty that every such collision will be inelastic. There exists a definite probability, which is a function of the velocity, that the collision will be of the inelastic type, and it is therefore necessary to introduce specific definitions for the probabilities of different processes which occur when an electron collides with an atom. These are as follows:

The *probability of collision*, P_c, is the number of collisions per unit electron current, per unit path length, per unit pressure at $0°$ C. Similarly, the *probability of excitation*, P_e, is the number of excited atoms, and the *probability of ionization*, P_i, the number of ions,—in each case, per unit electron current, per unit path length, per unit pressure at $0°$ C.

That $Pp.$, where p = pressure in mm., corresponds to an "absorption coefficient," and the reciprocal to a "free path," L, is evident from the following remarks by R. B. Brode: [2]

"The probability of a collision in a distance dx in a gas at a pressure p is $P_c p dx$. A current of electrons of strength I passing through the layer dx is decreased by

$$dI = -IP_c p dx.$$

Hence

$$I = I_0 e^{-P_c x p}, \qquad (16.57)$$

where I_0 is the initial electron current in the beam and I is the electron current after passing a distance x through the gas at a pressure p.

"The mean free path, L, is the average distance travelled before colliding and is given by $pL = 1/P_c = L_0$ the free path at unit pressure. The dimensions

---

[1] For detailed discussion of this topic see R. B. Brode, *Rev. Mod. Phys.*, **5**, 257 (1933).

[2] *Loc. cit.*, p. 258.

of P_c are $l^{-1}p^{-1}$ or $l^2l^{-3}p^{-1}$ or area, per unit volume, per unit pressure. P_c can therefore be considered *as the effective area for collision of all the atoms in a unit volume at unit pressure.* This is a very convenient description of the probability of collision, but one is not justified in ascribing this area to any particular part of the atom. In the equation for the decrease in current in the beam of electrons, the probability of collision enters in exactly the same way that an absorption coefficient enters in the decrease in intensity of X-rays or of light in passing through matter. Lenard called the coefficient P_c the absorbing power, and a large number of the workers in this field have used the designation absorption coefficient for this quantity. We know, however, that the electrons are for the most part scattered and that true absorption by attachment is a rare process."

Thus L_0P is to be regarded as a measure of the probability that excitation (or ionization) will occur at a single collision between the electron and atom. For instance, for a 22.0 volt in neon, the probability of ionization at a collision is 0.00134, or one collision out of 750 is effective in producing ionization.

In the previous remarks, the term *effective cross-section* was introduced, as a measure of efficiency of energy transfer at a collision, and in the present case, P_c, P_e and P_i can be replaced by q, the effective cross-section, by means of the relation,

$$q = 0.281 \times 10^{-16} P \text{ cm.}^2, \qquad (16.58a)$$

where the unit of pressure is one mm. of Hg at $0°$ C, and the unit of volume is 1 cc. The corresponding value of r in the relation, $q = \pi r^2$, is given by the relation,

$$r = 0.3 \times 10^{-8}\sqrt{P} \text{ cm.} \qquad (16.58b)$$

The last two equations yield results which may be compared with the kinetic theory values.

It should be noted that for electrons the mean free path in a gas is $4\sqrt{2}\,L_k$, where

$$L_k = \frac{1}{4\pi\sqrt{2}\,nr^2}$$

is the kinetic mean free path, n is the number of molecules per unit volume and r is the radius of a molecule.

In the following remarks there will be reviewed briefly the results obtained by a number of investigators on the variation of the probability coefficient with voltage (or velocity) of bombarding electrons.

C. Ramsauer [1] observed that for slow electrons in A, Kr and Xe, the value of P_c passes through a minimum at about 1 volt. This so-called *Ramsauer effect* is illustrated in Fig. 16.6.[2]

---

[1] *Ann. Physik*, **64**, 513 (1921).

[2] R. B. Brode, *loc. cit.*, Fig. 8.

Figures 16.7 and 16.8 [1] show values of P_c as a function of velocity $(v = \sqrt{2(e/m)V})$ for elements of Groups II and I respectively. At low velocities
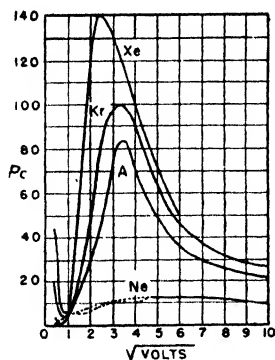
FIG. 16.6. Probability of Collision in Ne, Ar, Kr and Xe. The minimum at 1 volt illustrates the Ramsauer effect. (Brode)
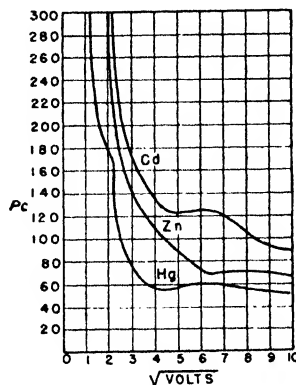
FIG. 16.7. Probability of Collision in Zn, Cd and Hg (Brode)

the effective cross-sections are greater than those calculated on the kinetic theory basis, but become comparable with the latter at higher velocities.
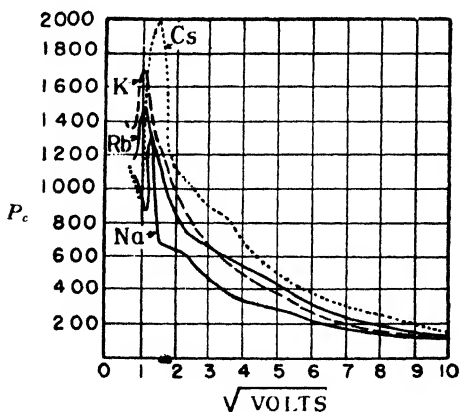
FIG. 16.8. Probability of Collision in Na, K, Rb and Cs (Brode)

The value of P_c for any given atomic species starts from zero at the excitation potential, passes through a maximum as the electron velocity is increased, and decreases more or less uniformly with further increase in electron velocity. Fig. 16.9 [2] shows the variation *with* V, of P_c for the two resonance states of Na. In this and similar investigations on other vapors, the value of P_c was obtained from observations on the loss in energy of the bombarding electrons as a function of V, in accordance with equation (16.53).

This method was used, for instance, by I. Langmuir and H. A. Jones [3] in determining values of P_c, P_i for electrons at higher voltages (30 to 250 volts) in a number of gases and vapors. A very full review of this work

[1] R. B. Brode, *loc. cit.*, Figs. 12 and 13.

[2] R. B. Brode, *loc. cit.*, Fig. 18.

[3] *Phys. Rev.*, **31**, 357 (1928).

and of other investigations on the subject has been published by K. T. Compton and I. Langmuir.[1]

W. B. Nottingham,[2] however, has used a photoelectric method to determine P_e. The radiation spontaneously emitted by the excited atoms causes the ejection of photoelectrons from a negatively charged electrode, and hence the photoelectric yield per primary electrons is a measure of P_e. Fig. 16.10 shows the effect of increased energy of bombarding electrons on the efficiency of excitation in mercury vapor. The excitation energies for the different terms of the mercury spectrum are indicated by the vertical lines. At 4.9 volts, the excitation to $^3P_2$ state sets in and reaches a maximum at about 5.6 volts. The decrease in P_e with further increases in voltage is masked by the excitation to the $^1P_1$ state which begins at 6.7 volts.

Fig. 16.9. Probability of Excitation of the 3 $^2P_{1/2, 3/2}$ Terms in Sodium (Lovenridge). (Curve A uncorrected for electron velocity distribution; curve B corrected for electron velocity distribution)

By measuring the total number of positive ions per primary electron, collected by a negative electrode, the value of P_i for mercury was determined as a function of accelerating potential as shown in Fig. 16.11 [3] in curve E_i. In-

Fig. 16.10. Probability of Excitation of Mercury as a Function of Electron Velocity (Nottingham)

[1] *Rev. Mod. Phys.*, **2**, 123 (1930).

[2] *Phys. Rev.*, **55**, 203 (1939). This gives references to many of the previous investigations on this subject.

[3] W. B. Nottingham, *loc. cit.*, Fig. 15.

FIG. 16.11.   Probability of Ionization of Mercury as a Function of Electron Velocity (Nottingham).   (Curve E_i is the uncorrected curve which includes multiple ionization; curve P_i gives the probability of ionization with loss of only one electron)

troducing a correction based on measurements by W. Bleakney [1] for the number of multiply-ionized atoms, the curve P_i is obtained, which gives the probability of ionization with loss of only one electron.

With regard to the efficiency of excitation it may be stated that in general it rises to a maximum within a volt or less of the critical voltage and then decreases with increasing energy.   Thus for sodium the probability that a 2.5 volt electron will cause excitation to the ^2P levels ($V_r = 2.12$ volt) at a collision, is 0.05 according to L. S. Ornstein and B. Baars [2] and 0.52 according to W. Christoph[3].

According to measurements by L. C. van Atta [4] the efficiencies of inelastic collisions in the rare gases are those given in Table 16.10.

TABLE 16.10

	Energy Loss	Transition	Yield
He	22.11	$1^1S_0 - 2^1P_1$	0.5 to 1.0×10^{-2}
Ne	16.68	$1^1S_0 - 2^1P_1$	$\sim 0.6 \times 10^{-2}$
A	11.57	$1^1S_0 - 2^3P_1$	$2 - 1 \times 10^{-2}$

The effective cross-sections for ionization at electron velocities which correspond to maximum efficiency, according to H. Kallmann and B. Rosen [5] are given in Table 16.11.

[1] *Phys. Rev.*, **35**, 139 (1930).

[2] *Proc. Amsterdam Acad.*, **34**, 1259 (1931).

[3] *Ann. Physik*, **23**, 51 (1935).

[4] *Phys. Rev.*, **38**, 876 (1931).

[5] *Physik. Z.*, **32**, 540 (1931).

TABLE 16.11

	Kinetic Theory value of q	q for Ionization		Kinetic Theory value of q	q for Ionization
A^+	27.2×10^{-16}	3.2×10^{-16}	H_2	18.1×10^{-16}	1.1×10^{-16}
A^{2+}	27.2	0.32	Hg^+	10	6.2
A^{3+}	27.2	0.01	Hg^{2+}	10	0.9
Ne^+	17.5	0.98	Hg^{3+}	10	0.2
Ne^{2+}	17.5	0.06	Hg^{4+}	10	0.04
He^+	11.1	0.51			

W. Penney [1] has calculated, by the methods of wave mechanics, the excitation probabilities by electron impact for the four P levels of Hg. The results obtained are shown in Fig. 16.12. At 10 volts, the relative values of P_e
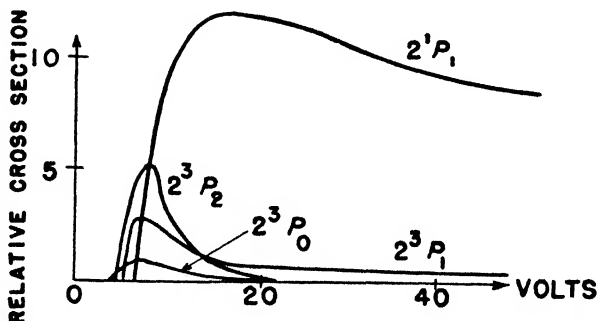
Fig. 16.12. Probability of excitation for the ^3P and $^1P_1$ States of Mercury as Calculated on Basis of Wave Mechanics (Penney)

are in the ratio 7.0 : 3.5 : 1.9 : 0.4 for the $^1P_1$, $^3P_2$, $^3P_1$ and $^3P_0$ levels respectively, but at higher voltages the values of P_e for the two metastable levels decrease rapidly to zero, as shown in the diagram. Penney's deductions are apparently in good agreement with experimental results observed by C. W. Ford.[2] The latter succeeded in separating the 4.9 volt excitation from the 5.5 volt excitation, but only for primary voltages of about 6 volts.

These results are interesting in view of the fact that we would expect the efficiencies for excitation of metastable states to be considerably smaller than those for excitation of ordinary excited states (from which spontaneous transitions can occur).[3] This is demonstrated by the fact that in the Franck-Hertz method for determining critical potentials, no discontinuities are observed at those voltages which correspond to excitation of the metastable states. Fur-

---

[1] *Phys. Rev.*, **39**, 467 (1932).

[2] *Ibid.*, **35**, 1187 (1930).

[3] W. Hanle and K. Larché, in E. Marx, Handbuch der Radiologie, vol. VI, part 1, p. 162; Akademische Verlagsgesell., Leipzig, 1933.

thermore, it follows from the considerations advanced by Klein and Rosseland that the probability for such excitation must be extremely low.

Actually it has been deduced by W. Elsasser [1] and H. Bethe [2] by wave mechanics methods that the probability of excitation on impact by *very fast* electrons is proportional to the Einstein probability coefficient for the spectral transition and inversely proportional to the kinetic energy of the electrons.

From measurements of the relative intensities of a spectral line as a function of electron voltage, R. Seeliger and a number of collaborators have determined the so-called *"optical excitation function,"* F_c.[3]   Figs. 16.13, 16.14 and 16.15
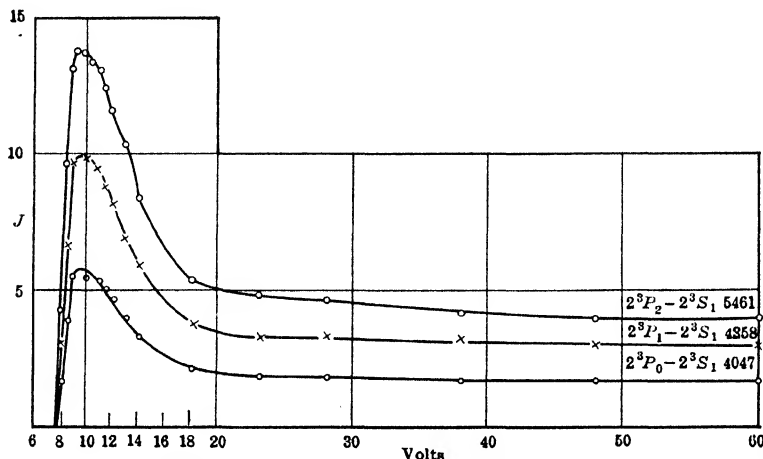
Fig. 16.13.   Optical Excitation Function for $^3P - {}^3S_1$ Lines in the Spectrum of Mercury

show plots of the excitation functions for triplet and singlet lines in the spectrum of mercury.   The excitation function for the resonance line $^3P_1 - {}^1S_0$ as determined by L. S. Ornstein, H. Lindemann and J. Oldemann [4] shows a maximum at 6.5 volts and resembles in that respect the function for the triplet series plotted in Fig. 16.12.

Assuming that the spectral line represents the only transition from the level k to j,

$$F_e = P_e A_{kj} = P_e/\tau, \qquad (16.59)$$

so that F_e is intimately related to P_c.   However, usually there are two or more

---

[1] *Z. Physik,* **45**, 522 (1927).

[2] *Ann. Physik,* **5**, 325 (1930).

[3] The earlier work on this topic has been reviewed by J. Franck and P. Jordan, p. 181, *op. cit.*   For a discussion of more recent work see R. Seeliger, Einführung in die Physik der Gasentladungen, J. A. Barth, Leipzig (1934), the review by W. Hanle and K. Larché, *Ergebn. exakt. Naturwiss.,* **10**, (1931), and a review by the same authors in Handbuch der Radiologie.

[4] *Z. Physik,* **83**, 171 (1933).
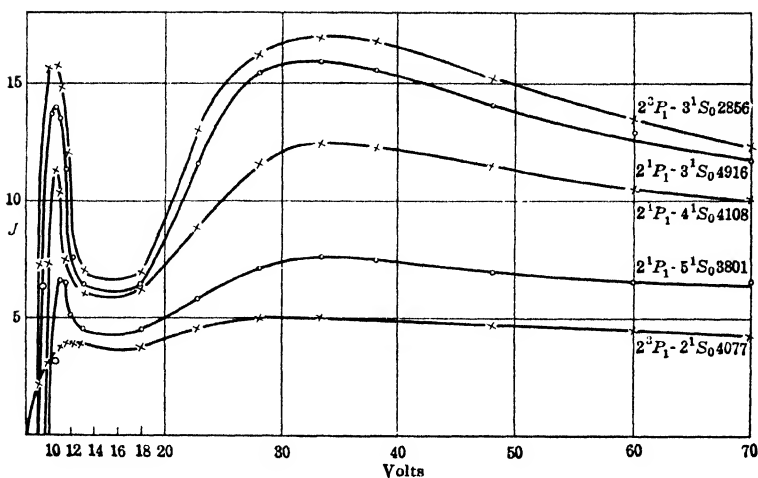
Fig. 16.14.   Optical Excitation Function for $^1P_1$–$^1S_0$ and ^3P–$^1S_0$ Lines
in the Spectrum of Mercury

transitions from the same level.   Furthermore, excited atoms in level k can
be replenished by transitions from above as well as by collisions of the second
kind.   Consequently, F_e cannot be given the same definite interpretation as
the excitation function, P_e.

When electrons (or atoms) collide with atoms the two particles suffer a
change in direction of relative motion.   This *scattering* occurs for both elastic
and inelastic collision.   The scattered current per unit current, per unit path
length, per unit pressure at $0°$ C., per unit solid angle in the direction θ, is
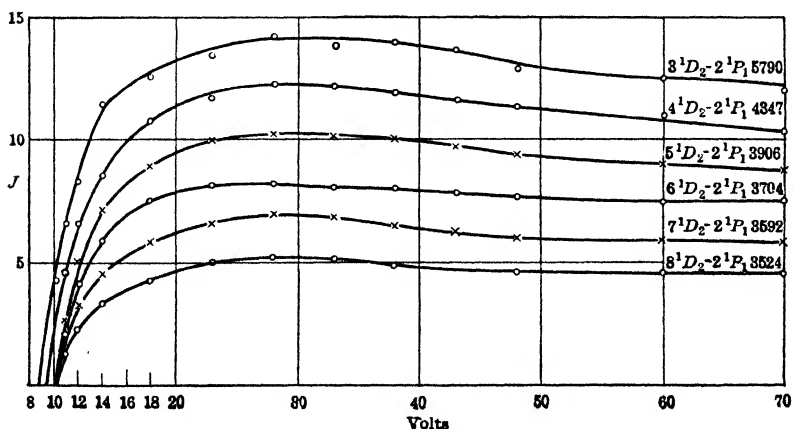
Fig. 16.15.   Optical Excitation Function for $^1D_2$–$^1P_1$ Lines in the Spectrum of Mercury

defined as the *probability of scattering* S. The probability of excitation, P_e, is related to the function S_e by the relation,

$$P_e = \int_0^\pi S_e 2\pi \sin \theta d\theta, \tag{16.60a}$$

and similarly

$$P_i = \int_0^\pi S_i 2\pi \sin \theta d\theta. \tag{16.60b}$$

The investigations on the measurement of S for both elastic and inelastic collisions have been reviewed by K. T. Compton and I. Langmuir [1] and also by R. B. Brode.[2] From a theoretical point of view such observations are of importance because of the information which they yield regarding the nature of the atomic field of force. A classic example of the importance of such an investigation is that carried out by Rutherford on the scattering of alpha particles, which led to the nuclear theory of atomic structure.

Because of these considerations the subject has received considerable attention from many theoretical physicists, such as M. Born, N. F. Mott, P. M. Morse and others,[3] who have applied the methods of quantum mechanics to the problem. In this manner the Ramsauer effect has been explained as a natural consequence of the wave properties of the electron. Some of the conclusions deduced in the case of these investigations have been mentioned previously. While it has been possible to calculate probability of excitation for some of the more simple atomic systems, the calculation is much more difficult in most cases.

Incidentally, the investigations on these probability coefficients as well as those on the life and concentration of excited (including metastable) atoms have proved of great significance in interpreting many of the observations on the characteristics of electric discharges in gases. This has been specially applicable to those discharges which are of practical importance as light sources.[4]

(9) **Thermal Excitation and Ionization**: The spectra observed for the radiation from stellar atmospheres and in experiments at such high temperatures as can be obtained in the laboratory are due to thermal excitation and ionization. Under conditions of temperature equilibrium for atoms, excited atoms, ions and electrons, the degree of excitation at any temperature is given in accordance with Boltzmann's law, as modified by Einstein, by equation (16.43). If in this equation we replace $E_k - E_j$ by the equivalent value of the energy difference in electron-volts, V, then the equation can be expressed in the form

[1] *Rev. Mod. Phys.*, **2**, 123 (1930).

[2] *Loc. cit.*

[3] A brief summary of the methods used and conclusions is given by R. B. Brode, *loc. cit.*, while a very comprehensive discussion has been given by P. M. Morse, *Rev. Mod. Phys.*, **4**, 577 (1932). Brode's review gives a list of other references to discussions of this topic.

[4] For discussion of this topic and bibliography see S. Dushman, *J. Opt. Soc. Am.*, **27**, 1 (1937), also C. G. Found, *Gen. Elec. Review*, **37**, 269 (1934).

of equation (16.45), that is,

$$\log Q = \log \left(\frac{N_j g_0}{N_0 g_j} \right) = - \frac{5040V}{T}, \tag{16.61}$$

where N_0 = concentration of atoms in normal state,

N_j = concentration of atoms in excited state j,

g_0 and g_j are the corresponding statistical weights,

V = energy in volts for excitation to state j.

If J_0 and J designate the values of this quantum number for the lower and upper states respectively, $g_0/g_j = (2J_0 + 1)/(2J + 1)$. Hence this ratio has a value of between 1 and about 0.1 for excited states which are of more usual interest.

From equation (16.61) it is possible to calculate values of Q, and hence values of N_j/N_0, as a function of T for any given value of V. Table 16.5 in Section 16(5) gives the results of such a calculation for excited states of Cs and Hg, and as pointed out in connection with this table, the degree of excitation is extremely low even at temperatures as high as 5000° K. for all but the very few atomic species, which like that of caesium, require relatively low values of V for excitation.
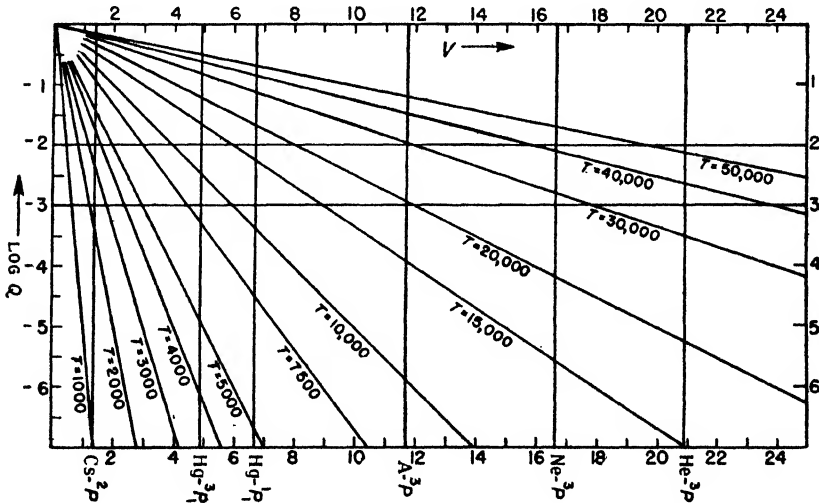
FIG. 16.16   Plots for Calculating Degree of Thermal Excitation of Atoms at Different Temperatures.   Log Q = log $(N_j g_0/N_0 g_j)$.   Two horizontal lines give values of T for $Q = 10^{-2}$ and 10^{-3} respectively.   The vertical lines correspond to selected excitation potentials.

Figure 16.16 which gives plots of log Q versus V for a series of values of T shows that for most gases and vapors, the temperatures required to attain values of Q of the order of 10^{-3} are considerably higher than those attainable in the laboratory.   The values of Q corresponding to 10^{-3} and 10^{-2} are indicated

by the two horizontal lines, and vertical lines have been drawn for values of V which correspond to some of the excited states mentioned in previous sections.

While equation (16.61) is applicable to the calculation of degree of excitation, it is also of interest to determine the degree of ionization at a given temperature. As the temperature increases to values comparable with $5040 V_i$ (say one-tenth or more of this value), the atoms dissociate into singly charged ions and electrons (that is into $M^+ + e$, where M designates the chemical symbol for the element). As the temperature is increased still higher, the dissociation takes the form $M^{2+} + 2e$, and finally, at extremely high temperatures, such as exist inside the stars, even the most tightly-bound electrons, such as those in the K-shell, are removed, and only nuclei and electrons are present. In fact, such stars are known and they are of interest because of their extremely high densities.

The degree of dissociation may be calculated by exactly the same type of relation as that developed on the basis of thermodynamical considerations for calculating equilibrium concentrations in chemical reactions. In this manner, M. Saha [1] derived an equation for the case of dissociation into a singly charged ion and electron which has the form,

$$\ln K_p = \ln \frac{p^+ p^-}{p} = -\frac{23054 V_i}{RT} + \tfrac{5}{2} \ln T + B, \qquad (16.62)$$

where p^+, p^- and p represent the pressures of positive ions, electrons, and undissociated atoms, respectively; R is the molar gas constant and B is a "chemical" constant. According to R. H. Fowler,[2]

$$B = \ln \left\{ \frac{(2\pi m)^{3/2} k^{5/2}}{h^3} \right\} + \ln G, \qquad (16.63)$$

where $G = g_e g_i / g_0$ and g_e, g_i and g_0 are the "weights" for the electron, positive ion and neutral atom respectively. Replacing R in equation (16.62) by the value 1.9869 cal. deg.$^{-1}$ mole^{-1}, k, m and h by their corresponding values, and converting to ordinary logarithms, this equation assumes the form,

$$\log K_p = \log \left(\frac{\alpha^2 p}{1 - \alpha^2} \right) = \log G + \bar{1}.5231 + \tfrac{5}{2} \log T - \frac{5040 V_i}{T}, \qquad (16.64)\,[3]$$

where α = degree of dissociation at pressure p, in *dynes cm.$^{-2}$*

In terms of concentration (n) expressed in atoms (ions, or electrons) per cc., the equilibrium constant is given by the relation

$$\log K_n = \log \left(\frac{n_e n_i}{n_0} \right) = \log K_p - \log (kT)$$

$$= \log G + 15.3831 + \tfrac{3}{2} \log T - \frac{5040 V_i}{T}. \qquad (16.65)$$

---

[1] *Proc. Roy. Soc.*, [**A**], **99**, 135 (1921). This equation has also been discussed very fully by F. M. *op. cit.*, Chapter X, and in ref. R. C., p. 147.

[2] Statistical Mechanics, 2d ed., p. 372, Univ. Press, Cambridge, England (1936).

[3] Since 1 atm. = 1.01325 × 10⁶ dynes cm.$^{-2}$, the second term on the right-hand side of this equation is equal to $\bar{7}.5174$ for p in atmospheres, and to $\bar{4}.3982$ for p in mm. of Hg at 0° C.

This relation has been verified by I. Langmuir and K. H. Kingdon [1] from measurements on the ionization of cesium atoms which strike the surface of tungsten or thoriated tungsten filaments at high temperatures. In this case $V_i = 3.88$ volts, $g_e = g_0 = 2$ and $g_i = 1$ and hence $G = 1$. Consequently equation (16.65) reduces to

$$\log K_n = 15.3831 + \tfrac{3}{2} \log T - 19530/T.$$

Thus for $T = 1200°$ K., $K_n = 5.34 \times 10^3$, and for n_0 corresponding to 10^{-2} dyne cm.$^{-2}$, the degree of dissociation is 0.00095, that is, about 0.1 per cent.

Further work on the thermal ionization of vapors has been carried out by T. J. Killian [2] with rubidium and potassium, by E. Meyer [3] with potassium, by N. Morgulis [4] with sodium, and by B. N. Srivastava with barium [5] and strontium.[6] In all cases the results agree, within the limits of experimental errors, with the theoretical relations.

Equation (16.64) shows that α increases with increase in temperature and with decrease in pressure. For low values of α, this equation may be expressed in the form,

$$2 \log \alpha = \log G - 6.4826 - \log p + \tfrac{5}{2} \log T - 5040 V_i/T, \quad (16.66)$$

where p is expressed in *atmospheres*.

For double ionization P. D. Foote and F. L. Mohler have derived a similar relation,[7] while R. H. Fowler has given more general expressions for still higher stages of ionization.[8]

Tables 16.12 and 16.13 give the percentage dissociation of calcium and atomic hydrogen at a series of temperatures and pressures, as deduced by means of equation (16.64). The values of V_i, g_i, g_0 and G for these two elements are as follows:

	V_i	g_i	g_0	G
H.....	13.59	2	2	2
Ca.....	6.11	2	1	4

The values of $5040 V_i$ for calcium and hydrogen are 30,790° and 68,480° K. respectively, the ratio being 2.22, and it will be observed that to obtain the same

[1] *Proc. Roy. Soc.*, [A], **107**, 61 (1925).

[2] *Phys. Rev.*, **27**, 578 (1926).

[3] *Ann. Physik*, **4**, 357 (1936).

[4] *Phys. Z. Sowjetunion*, **5**, 221 (1934).

[5] *Proc. Roy. Soc.*, [A], **175**, 26 (1940).

[6] *Ibid.*, **176**, 343 (1940).

[7] Ref. F. M., Chap. VII. They used the value 6.69 instead of that given in equation (16.66).

[8] *Op. cit.*, Section 15.31.

TABLE 16.12

Thermal Ionization of Calcium Expressed in Percentage

T	$P = 1$	10^{-2}	10^{-4}	10^{-6} atm.
2,000	3.1×10^{-5}	3.1×10^{-4}	3.1×10^{-3}	3.1×10^{-2}
3,000	1.87×10^{-2}	1.87×10^{-1}	1.87	18.3
4,000	5.18×10^{-1}	5.18	46.0	76.7
5,000	4.02	37.3	97.0	
7,500	57.9	91.4	Ionization > 99	
10,000	95.8			

TABLE 16.13

Thermal Ionization of Hydrogen Expressed in Percentage

T	$P = 1$	10^{-2}	10^{-4}	10^{-6} atm.
5,000	5.41×10^{-4}	5.41×10^{-3}	5.41×10^{-2}	5.41×10^{-1}
7,500	1.54×10^{-1}	1.54	15.2	83.9
10,000	3.06	29.3	95.0	
12,500	19.2	88.9	Ionization > 99	
15,000	57.5			

degree of dissociation the temperature required in the case of atomic hydrogen is approximately twice that required for calcium.

Such calculations of thermal ionization as a function of temperature have been used by R. H. Fowler and E. A. Milne [1] to deduce temperatures and pressures in the reversing layers of stellar atmospheres from observations on the intensities of absorption lines in the spectra emitted.[2]

(10) **Other Methods of Excitation and Ionization:** While excitation and ionization are most efficiently produced by electron impact, these effects may also be brought about by collisions between ions and neutral atoms and even by collisions between neutral atoms, if their relative energy exceeds a critical value.

Ionization of neutral atoms by high speed ions sets in at a definite potential (which is considerably higher than the value for ionization by electrons), increases linearly with voltage for a certain range, passes through a maximum, and then decreases very slowly with further increase in voltage.

[1] Fowler, *op. cit.*, Chap. XV.
[2] See also remarks by F. M., *op. cit.*, p. 170 *et. seq.*

The ionization of rare gas atoms by alkali ions with velocities in the range 100 to 600 volts has been determined by a number of investigators.[1] In general the threshold value for ionization varies, according to Varney, from 77 volts for Cs^+ in xenon to about 400 volts for Li^+ and Na^+ in krypton. The threshold values observed by previous investigators are apparently somewhat higher. For Cs^+ ions with an energy of 500 volts, the number of ions per unit path length at 1 mm. pressure, in xenon, may be as high as 3.11.

Of the experimentally observed ionizing energy, the fraction $m_i/(m_a + m_i)$ is necessary for conservation of momentum and energy, and the fraction $m_a/(m_a + m_i)$ is available for ionization. In these expressions m_a = mass of atom, m_i = mass of ion. According to Varney,[2] "the reduced energy thus obtained for an ionizing collision between an ion having A electrons and an atom with B electrons was almost identical with that obtained when the ion had the B electrons and the atom had A electrons." Furthermore, it was observed that "the reduced energy was less when an ion and an atom had the same number of electrons than when they had different numbers." Another interesting result observed is that the ionization of other than the rare gases by positive alkali ions is not more than about 1 per cent of that obtained with K^+ in A.

In the second paper referred to above, Varney has also investigated the ionization of rare gases by their own ions. The high efficiency of ionization of rare gases by their ions was first observed by Kallmann and Rosen [3] and Varney's results are in agreement with these observations. The threshold values for ionization in the four gases investigated were as follows:

	Observed Values	Reduced Values
Ne in Ne	74 volts	37 volts
A in A	48	24
Kr in Kr	40	20
Xe in Xe	35	17.5

As Varney remarks, "These values are surprisingly low, being in each case only a few volts above the actual ionization potentials of the gases. . . . The results are almost half those for the alkali ions in the noble gases." No ionization was observed of one gas by neutral atoms of another gas, where the neutral atoms were obtained by first neutralizing the ions in one chamber and then letting them enter a second chamber containing the different gas.

Closely allied to the phenomena of ionization of neutral atoms by high speed ions is that of *electron transfer* between slow speed ions and atoms. Following up earlier observations by Harnwell [4] on discharges in mixtures of He and Ne, which could be interpreted by assuming that He^+ and Ne may inter-

[1] R. N. Varney, *Phys. Rev.*, **47**, 483 (1935). This gives references to the work of previous investigators on this topic.

[2] *Phys. Rev.*, **50**, 159 (1936).

[3] *Z. Physik*, **61**, 61 (1930).

[4] *Phys. Rev.*, **29**, 683 (1927).

change electrons, thus producing Ne^+ and He, other investigators made similar observations in other cases.   F. London [1] has discussed this effect, which has its analogy in the reaction,

$$\text{Hg (excited)} + \text{Na} \rightarrow \text{Na (excited)} + \text{Hg},$$

as a bimolecular reaction, for which the probability of occurrence may be deduced from the wave functions for the two particles.   Also H. Kallmann and B. Rosen [2] have shown by application of the mass spectrograph that such energy transfers may occur not only between, say, A and A^+, but also between A^{++} and A^+.   In the case of collisions between A^{++} and A, F. Wolf [3] has concluded from observations made by the same method that *transfer of two electrons* is *highly probable.*[4]

As is well known, canal rays and high speed protons and deuterons produce both excitation and ionization, and similar results are observed with alpha particles.[5]

The production of light as a result of *recombination* of ions and electrons and the reverse process, that is, the ionization of atoms or molecules by light (*photo-ionization*) has been discussed by F. L. Mohler.[6]

We shall consider first the phenomena associated with recombination. The rate of recombination follows a law of the form

$$- dn_i/dt = vq(v)n_i n_e = \alpha n_i n_e, \tag{16.67}$$

where n_i and n_e denote concentration of ions and electrons respectively, v is the relative speed of the electron, $q(v) = \pi a^2$ is the "target area," and α is the coefficient of recombination.

The frequency, ν, of radiation emitted as a result of the collision is given by the relation

$$h\nu = h\nu_i + \tfrac{1}{2}mv^2, \tag{16.68}$$

where $\nu_i = (e/h)V_i$, and the term $\tfrac{1}{2}mv^2$ is the kinetic energy of the colliding electron.   Since, in general, the electrons have a Maxwellian distribution, corresponding to a continuous range of values of v, the radiation emitted exhibits a continuous spectrum extending towards higher frequencies beyond ν_i, that is, towards the violet and ultraviolet.   Such spectra have been observed quite frequently in electric discharges in hydrogen and other gases and vapors.

[1] *Z. Physik*, **74**, 143 (1932).

[2] *Ibid.*, **64**, 806 (1930); **61**, 61 (1930).

[3] *Ann. Physik*, **34**, 341 (1939) and preceding papers.

[4] See also further remarks by E. J. B. W., *op. cit.*, Chap. 3.

[5] See review by W. Hanle and K. Larché, pp. 198–203, Handbuch der Radiologie, vol. 6, part 1 (1933).   More recent work in this field has also been reviewed by Hanle in *Die Physik*, **6**, 33 (1938).

[6] *Phys. Rev.* (Supplement), **1**, 216 (1929).   See also A. v. Engel and M. Steenbeck, Elektrische Gasentladungen, pp. 211–223, Julius Springer, Berlin (1932).

Instead of recombining to form an atom in the normal or ground state, the ion and electron may give rise to an excited atom. If ν_e denote the frequency corresponding to a transition from this level to the normal, a continuous spectrum is observed extending over a range of frequencies beyond this value.

As Mohler states, "Various lines of evidence indicate that under most low-pressure discharge conditions recombination in free space is negligible compared to loss of ions by diffusion to walls and electrons." But under certain special conditions recombination spectra are obtained. "The intensity $I(\nu)d\nu$, in a continuous band at a given frequency interval beyond the limits depends on the concentration of electrons of the corresponding speed, on the concentration of ions, and on the recombination coefficient for capture into the level concerned. Since the number of quanta emitted in unit volume equals the number of recombinations, we have corresponding to equation (16.67),

$$I(\nu)d\nu/h\nu \,=\, vq(vv_i)n_in_eF(v)dv, \tag{16.69}$$

where $q(vv_i)$ represents the 'cross-section' for recombination, which is a function of v and ν, and $F(v)dv$ gives the fraction of the electrons in a range corresponding to dv."

Measurements by Mohler on the intensity of the radiation beyond the ^2P limit of cesium show that

$$vq(v, {}^2P) \,=\, \frac{C_1}{\nu^2\sqrt{\nu - \nu_i}} \,=\, \frac{C_2}{\nu^2v^2}, \tag{16.70}$$

where C_1 and C_2 are constants.

This relation gives the variation with frequency and kinetic energy of electrons, in the value of the coefficient of recombination, and shows that the value of this coefficient decreases with both increase in frequency and increase in electron temperature (since this is a measure of v^2). The effective collision area for capture of 0.2 volt electrons into a ^2P level is 6×10^{-21} cm.^{2}, which is considerably less than the kinetic theory cross-section (about 10^{-15} cm.^{2}). This indicates that the efficiency of light emission as a result of recombination is extremely low.

The reverse reaction, which may be written in the form

$$h\nu + \text{atom} \rightarrow \text{ion} + \text{electron},$$
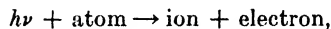
has also been investigated. On the basis of the principle of microscopic reversibility, there should be a relation between the absorption coefficient for radiation (k) of frequency $\nu > \nu_i$ and the cross-section for capture of electrons by ions. In the X-ray region, k varies as $Z^4\lambda^3$ where Z is the effective nuclear charge. The absorption coefficient for continuous radiation beyond the $^2S_{1/2}$ limit for alkali metals, as measured by Mohler and others, is about 10^{-19}.

A direct determination of k has been made by Foote and Mohler from measurements of the current produced in an ionization chamber by a beam of

radiation of known energy flux (photo-ionization). Fig. 16.17 [1] shows the relative sensitivity $(k/h\nu)$ as a function of λ for caesium vapor. The maximum occurs at the limit 3184 Å, which corresponds to 3.89 volts, the ionization potential of Cs.
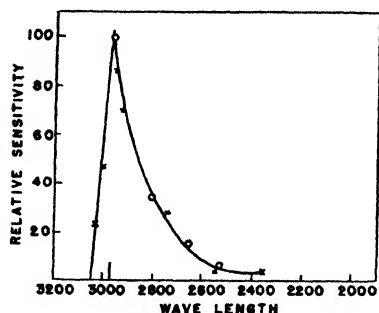
FIG. 16.17. Relative Ionization of Cs as a Function of Wave Length of Incident Radiation. (The limit occurs at λ corresponding to V_i = 3.89 for Cs)

(11) **Excitation of Inner Electrons:** Closely allied to these phenomena of photo-ionization are some extremely interesting observations by H. Beutler [2] on the absorption spectra obtained with metallic vapors and the rare gases in the extreme ultraviolet region extending from 1200 to 600 Å. A continuous spectrum in this range is emitted, as J. J. Hopfield [3] has shown, by passing a condenser discharge in helium at a pressure of a few millimeters.

In an ordinary arc discharge such as that in mercury vapor, the line spectrum is due (as shown in Fig. 1.6) to excitation of one of the outer s-electrons in the configuration $(5d)^{10}(6s)^2$, and the terms obtained are represented by the configurations $(5d)^{10}6s \cdot ml$, where $l = s,\, p,\, d,\, \cdots$ and m is the total quantum number associated with the electronic orbital. Such a spectrum Beutler designates by Hg_I^a. As mentioned in a previous section, the transitions from the resonance states of mercury, that is $\lambda2537$ and $\lambda1849$, may also be observed as absorption lines when the vapor is exposed to radiation of these wave lengths. However, it is possible to excite one of the $5d$ electrons and thus obtain transitions from terms corresponding to the configuration $(5d)^9(6s)^2 \cdot ml$, where l and m indicate the type of orbital. The spectrum obtained in this manner is designated by the symbol Hg_I^b.

That the series of terms in this spectrum are due to excitation of an electron in the d-shell is evidenced by the fact that the limits of the series are identical with terms in the spark spectrum of the atom. Thus in the case of Hg, this spectrum would be that of Hg_{II}.

Figure 16.18 [4] illustrates the relation between the three sets of spectral terms for an alkali metal (configuration p^6s). The system I^a represents, in a condensed form, the four series of doublet levels observed in the arc spectrum of the atom, for which the limit corresponds to the configuration p^6.

On the other hand, if one of the p-electrons is excited to different s-states, the result is the system of terms, shown as I^b, for which the limit corresponds to the removal of the p-electron, that is, to the configuration p^5s.

[1] Mohler, *Phys. Rev.* (Supplement), **1**, 220 (1929).

[2] *Z. Physik*, **86**, 495 (1933); **93**, 177 (1935) and in a number of other papers published during this period. A review of this work is given by A. G. Shenstone, *Reports on Progress in Physics*, **5**, 210 (1938).

[3] *Phys. Rev.*, **35**, 1133 (1930); **36**, 784 (1930).

[4] *Z. Physik*, **86**, 503 (1933).

The ground state for the spark system is the ionized alkali atom, which has the neon-like configuration p^6. By excitation of one of these p-electrons, we obtain as the resonance state, the configuration p^5s, and, by further excitation, the doubly ionized atom which is represented by the configuration p^5, as shown in the system of levels designated II.

Thus we may obtain the limit p^5s of the system I^b in two ways: (1) By ionization we pass from p^6s to p^6, and then excite one of the p-electrons of the ion to state p^5s. (2) As a result of absorption of a quantum of sufficient magnitude we get from p^6s to p^5s directly.

Let us now consider a configuration of the type $d^{10}s^2$ (such as that of Zn, Cd, or Hg). In this case we can again obtain the configuration d^9s^2 in two ways: (1) By absorption of a quantum we can pass directly from one state to the other. This is analogous to process I^b in the previous case. (2) By ionization of $d^{10}s^2$ we obtain $d^{10}s$, and then by excitation of a d-electron we obtain the state d^9s^2. This may be designated process II^b, since it is essentially an application of process I^b to the ion, instead of to the neutral atom. Hence, in presence of two s-electrons, the limit of the I^b spectrum is identical with a term in the II^b spectrum.

In the case of Zn ($3d^{10}4s^2$) we would expect, therefore, a series of absorption lines converging to a limit corresponding to the energy of removal of a $3d$ electron. These series would be associated with terms of the spectral type $3d^94s^2 \cdot mp$. Using Hopfield's continuum in helium, Beutler has actually observed the series of lines corresponding to the transitions $(3d^{10}4s^2)^1S_0 - (3d^94s^2 \cdot mp)\ ^3P_1^0, \ ^1P_1^0, \ ^3D_1^0$, where m varies from 4 to 12. "But," as Shenstone remarks,[1] "there is no reason why we should confine ourselves to a consideration of the $3d$ and $4s$ electrons. The excitation of any other electron will lead to similar results. This means that the X-ray absorption spectrum of an
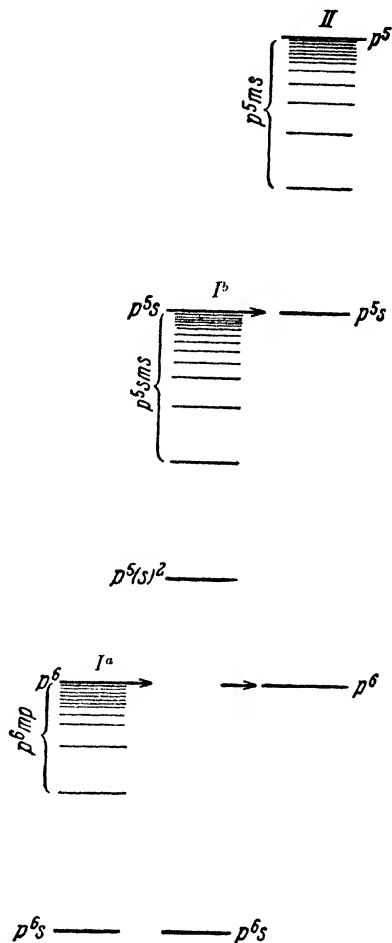
Fig. 16.18. Illustrating Spectra Obtained by Excitation of Outer s-Electron (I^a), of one of the Next Inner p-Electrons (I^b), and of the p-Electron in Ionized State (II) of Alkali Atom (Beutler)

[1] *Loc. cit.*

element in the gaseous state should consist of a set of absorption edges, each one of which has on its long wave length side a series of absorption lines. An indication of such lines has been found by D. Coster in argon."

These observations show that X-ray and optical spectra are of intrinsically the same nature. To illustrate this let us again consider the case of Zn, for which the complete configuration (as shown in Table 13.2) is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$. Ordinary optical states are due to excitation of one or both of the $4s$ electrons. The terms in the arc spectrum converge to the limit which corresponds to the removal of one $4s$ electron. The first enhanced spectrum is obtained by excitation of the second $4s$ electron. But, as described above, it is also possible to obtain absorption lines due to removal of one of the $3d$ electrons, and theoretically, at least, it should be possible to obtain other absorption spectra which are associated with the removal of one of the $3p$ or one of the $3s$ electrons, and so forth. This brings us into the X-ray region of absorption spectra and it follows that the absorption edges which correspond to the removal of L_I, L_{II}, L_{III} or M_I electrons and so forth, should exhibit a fine structure due to terms in the series for which these levels are the convergence limits. As Beutler points out, it is difficult to observe these lines because of the narrow region (only a few volts in extent) in which they occur. Nevertheless, Coster and other investigators have actually obtained evidence for the occurrence of this fine structure near the absorption limits.

It will be observed that the terms observed by Beutler (see Fig. 16.18) are above the normal ionization potential of the atom. We have thus a continuous spectrum upon which are imposed the discrete levels due to excitation of the inner electron. "Now," as Shenstone points out, "if an atom finds itself in a discrete state above the ionization point, it can ionize itself automatically with no change in its angular momentum vectors if there is a continuum with exactly the same characteristics." The probability of *auto-ionization*, as this effect is designated, will therefore govern the "life" (τ) of these discrete states. However, this problem has not yet been considered to any extent, from the theoretical aspect.

Beutler has observed series, similar to that described above for Zn, in the case of a number of other atoms, e.g. Hg, Cd, Cs, Rb, Tl, A, Kr and Xe.[1]

Figure 16.19 [2] shows the series of terms obtained in absorption for A, Kr and Xe, and the corresponding wave numbers represent the energy with respect to the ground states which correspond to the $^1S_0$ electron configurations $3p^6$ for A, $4p^6$ for Kr, and $5p^6$ for Xe. The ionization energies correspond to the $^2P^0_{3/2}$ terms, and the new terms between the latter and the $^2P^0_{1/2}$ terms correspond to a series of continua with sharp absorption edges. As will be observed these terms exhibit a diffuse structure and the lines associated with transitions from these terms to the lower levels show sharp absorption edges with pronounced shading towards the shorter wave lengths. The term $^2P^0_{1/2}$ represents a metastable state of the rare gas ion which results from the jj-coupling of

[1] Details are given by A. S. Shenstone, *loc. cit.*

[2] H. Beutler, *Z. Physik*, **93**, 177 (1935).

$p^5{}_{1/2} + s_{1/2}$ and $p^5{}_{1/2} + d_{3/2, 5/2}$. Of these terms only the two series for which $J = 1$, can combine with the normal (p^6) $^1S_0$ term.

Evidently these terms beyond the ionization limit are fairly stable with respect to the dissociation into an ion and electron.
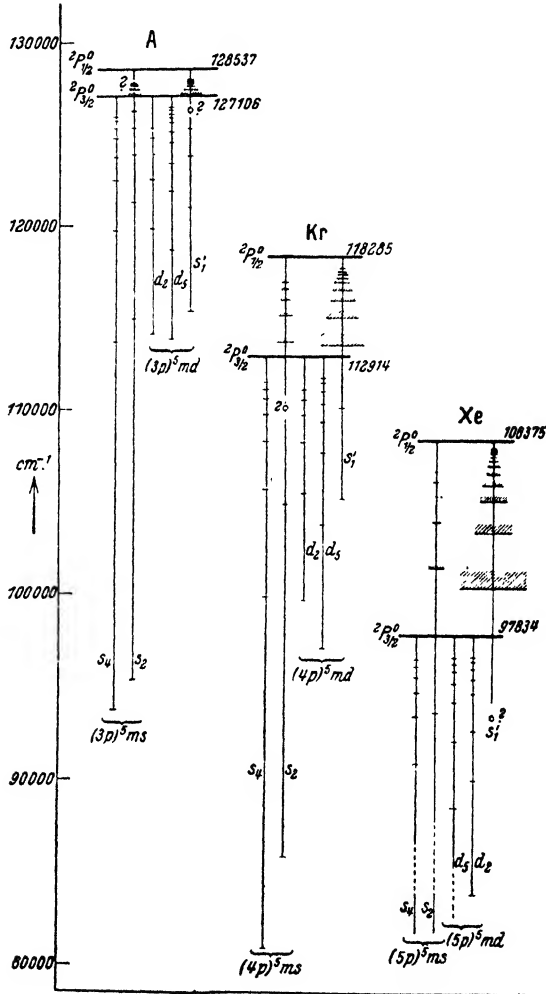
FIG. 16.19. Negative Terms Obtained for A, Kr and Xe by Absorption of Radiation in the Far Ultraviolet

If one considers, as Shenstone points out, the possibilities of observing spectral series due to transitions of other electrons in the shells located between the outer or valence shells and the innermost (K, L, etc.) shells, it is evident

that this line of investigation should yield an extremely interesting extension of our present knowledge in the field of spectroscopy.

Incidentally, it will also be recognized that there is an intimate connection between the observations described above and those described previously in Section 15(3) which arise from transitions of two electrons. Thus, it should be possible, in the case of Zn to observe lines due to transitions from a state $3d^9 4s^2 \cdot mp$ to a state $3d^{10} 4s \cdot ns$.

By analogy with the observations on absorption of resonance lines it would be expected that excitation of *inner* electrons to higher levels might be obtained as a result of electron impact just as well as by absorption. Some recent observations by A. H. Lee [1] on the energy losses of high speed electrons (accelerated by about 200 volts) in the vapors of zinc, cadmium and mercury, have been interpreted by him as due to the excitation of inner electrons by electron impact. The energy losses exceed the ionization potentials and the only simple explanation is, apparently, that the incident electrons excite some of the inner electrons to levels of the same type as those postulated by Beutler to explain his observations on ultraviolet absorption lines. This is illustrated by the data in Table 16.12. The nature of the transition is given in the second column, and the corresponding difference in energy in the third column. The last column gives the observed ultraviolet ionization potentials as deduced from the energy loss suffered by the impacting electrons.

TABLE 16.12

Element	Ultraviolet Absorption Line	Values in Observed	
		Volts	U.I.P.
Zn	$3d^{10}4s^2\,{}^1S_0\ -\ 3d^94s^24p^3P_1$	11.68	11.50
Cd	$4d^{10}5s^2\,{}^1S_0\ -\ 4d^95s^25p^3P_1$	12.76	12.80
Hg	$5d^{10}6s^2\,{}^1S_0\ -\ 5d^96s^26p^3P_1$	10.95	10.98
	$5d^{10}6s^2\,{}^1S_0\ -\ 5d^96s^27p^1P_1$	13.06	13.06

Thus, in the first case, the incident electron excites one of the inner *d*-electrons and gives rise to a $^3P_1$ state. The energy required for this excitation from the ground ($^1S_0$) state as calculated spectroscopically is 11.68 volts, and actually there is an observed energy loss for the high speed electrons of 11.50 volts. It will be observed that the corresponding values of the normal ionizing potentials (that required to remove one of the *s*-electrons from the ground state) for Zn, Cd and Hg are respectively, 9.39, 8.99 and 10.43.

17. Magnetic Properties of Atoms and Ions in Relation to Spectral Type

In section 4(3) the Stern-Gerlach experiments were described, which yield direct information on the magnetic properties of atoms in the normal state.

[1] *Proc. Roy. Soc.* [A], 173, 569 (1939).

For a state of quantum numbers, S, L and J, the component of the magnetic moment in the direction of the field is given by

$$\mu = Mg\mu_B, \tag{3-29}$$

where

$$\mu_B = \text{Bohr magneton} = \frac{eh}{4\pi mc} = 9.2720 \times 10^{-21} \text{ erg gauss}^{-1},$$

$$M = J, J - 1, \cdots - J,$$

and

$$g = 1 + \frac{J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)}. \tag{12.11}$$

Table 17.1 gives a list of values of μ as deduced by Stern and Gerlach for a number of elements investigated by them. It will be observed that these values are in agreement with the values of L, S and J assigned to the atoms on a spectroscopic basis.

<div align="center">TABLE 17.1</div>

Atoms	(μ/μ_B) Observed	Spectral Terms	Mg
Zn, Cd, Hg⎫ Pd, Sn, Pb⎭	0	$^1S_0$, $^3P_0$	0
H, Li, Na, K⎫ Cu, Ag, Au⎭	1	$^2S_{1/2}$	± 1
Tl	$\frac{1}{3}$	$^2P_{1/2}$	$\pm \frac{1}{3}$

It follows that in a magnetic field, atoms for which μ is zero should be diamagnetic, while those for which μ is not equal to zero should exhibit paramagnetism. We shall therefore consider more fully the manner in which the paramagnetic susceptibility per atom, χ, may be calculated for a vapor or gas constituted of paramagnetic atoms. At any given temperature T of the gas, the atoms will be distributed in the different states of quantum numbers M in accordance with the Boltzmann distribution law. That is, the fraction of the atoms in state M will be given by the relation

$$f_M = Ce^{\mu_M H/kT}, \tag{17.1}$$

where

$$C = \frac{1}{\sum_M e^{\mu_M H/kT}} \tag{17.2}$$

and the summation is extended over all the possible values of M for each value of J, corresponding to the different multiplet levels.

By definition,

$$\chi = \frac{\mu}{H},$$

and in the present case, this assumes the form,

$$\chi = \frac{1}{H} \frac{\sum \mu_M e^{\mu_M H/kT}}{\sum e^{\mu_M H/kT}}$$

$$= \frac{g\mu_B}{H} \frac{\sum M e^{\mu_M H/kT}}{\sum e^{\mu_M H/kT}}. \tag{17.3}$$

Let us consider the case for which $h\Delta\nu$, the difference in energy between the lowest pair of multiplet levels (which are given by successive values of J) is *large compared to kT*. (Thus for $T = 300$, $kT = 4.14 \times 10^{-14}$ erg $= 2.59 \times 10^{-2}$ volt $= 209$ cm^{-1}.) Then the summation has to be taken only over the M states for the lowest J level. Of these $2J + 1$ states, the lowest states, that is, those with negative values of M are more densely populated (because of the Boltzmann distribution law) than those with higher vaiues of M. "This means," as Herzberg points out,[1] "that the *atoms align preferentially with their magnetic moment in the field direction,* as would be expected. The stronger the magnetic field, the greater will be the energy difference for the various orientations in the field and, therefore, the greater the difference in the number of atoms occupying each state. For a given field, the difference in these numbers will be greater, the lower the temperature, since the arrangement of the atoms will be less hindered by unordered heat motion. The fact that in presence of a magnetic field, on the average, more atoms will align with their magnetic moments parallel to the field direction than antiparallel to it, results in a *magnetic moment per unit* volume $\chi n H$ (where n = number of atoms per unit volume) whose action is added to an external field and which can be determined experimentally. The gas is *paramagnetic.*"

We may now proceed with the derivation of what is known as Curie's law. For values of $\mu_M H \ll kT$, that is, for those cases in which the energy associated with each of the $2J + 1$ orientations in the field is small compared to the thermal energy kT (hence for values of T which are not very low),[2] equation (17.3) is reduced to the relation,[3]

$$\chi = \frac{(g\mu_B)^2}{kT} \cdot \frac{\sum M^2}{2J + 1} = \frac{J(J + 1)(g\mu_B)^2}{3kT}. \tag{17.4}$$

This may be written in the form,

$$\chi T = \frac{\mu_B^2 g^2 J(J + 1)}{3k} = \frac{\mu^2}{3k} = C, \tag{17.5}$$

---

[1] Ref. G. H., p. 205.

[2] Thus for H = 10,000 gauss, μ_M must be considerably less than 4.14×10^{-18} erg gauss^{-1}, that is, less than 447 times μ_B.

[3] The remarks on the derivation of equations (17.4) and (17.5) are based on the comprehensive discussion by E. C. S., *op. cit.*, p. 285 *et seq.*

where μ is the effective magnetic moment per atom, and C is a constant for any given gas or vapor.

In terms of *molar susceptibility*,

$$\kappa = \chi N,$$

where N is the Avogadro number; hence

$$\kappa T = \frac{\mu^2 N^2}{3R} = C_M, \tag{17.6}$$

where $C_M = $ constant.

Equation (17.6) which states that for any given paramagnetic gas, κ varies inversely as T, is known as Curie's law, and C_M is known as the *Curie constant.* It follows from equations (17.6) and (17.5) that,

$$\mu = \sqrt{3\kappa C_M/N} = 10^{-20} \times 2.593 \sqrt{C_M}, \tag{17.7}$$

that is,

$$p_B = \mu/\mu_B = 2.799 \sqrt{C_M} = g\sqrt{J(J+1)}. \tag{17.8}$$

Therefore it is possible to deduce values of μ from measurements of the Curie constant.

While equation (17.4) has been verified within the limits of experimental error by measurements made on the vapors of alkali metals, the most important tests have been obtained from measurements on paramagnetic ions in solution and in crystals. For the lowest state of an ionized atom it is possible, as mentioned previously, to deduce the type of spectral term from a knowledge of the electron configuration, and consequently it is possible to calculate the value of the magnetic moment μ, or the ratio μ/μ_B. In the case of ions such as those of Na^+, Ca^{++}, O^{--}, Cl^-, and so on, the electron configuration is the same as that of a rare gas atom, and consequently $\mu = 0$. However, in the case of elements of the first long period, where the added electrons enter into $3d$ or $4p$ shells, and in the case of the rare earths, where the added electrons enter into $4f$ shells, the value of J for the ions is not equal to zero. Consequently these ions should exhibit paramagnetic susceptibility,—a conclusion which was first pointed out by A. Sommerfeld [1] and verified on the basis of existing observations. F. Hund [2] also applied these considerations to the calculation of the magnetic moments of ions of the rare earths and showed that the experimentally observed values of χ are in very good agreement with those derived by means of equation (17.4).

For instance, the configuration of Gd (see Table 13.2) is as follows: 46 electrons in shells $1s$ to $4d$, 7 electrons in shell $4f$, 8 in $5s$ and $5p$, 1 in $5d$ and 2 in $6s$. The configuration of the tervalent ion, Gd^{3+} is obtained by removing the last three electrons. For the electron configuration thus obtained (in

---

[1] *Z. Physik,* **19,** 221 (1921); see also Atombau, pp. 630–643.

[2] *Z. Physik,* **33,** 855 (1925); see also Linienspektren, p. 179.

which only the $4f$ shell is incomplete), the spectral term is $^8S_{7/2}$, and the corresponding value of p_B as deduced by Hund from equation (17.8) is 7.94. The corresponding experimental value is 8.0. Table 17.1 [1] gives a comparison between calculated and observed values of p_B for ions of the rare earths.

<div align="center">TABLE 17.1</div>

<div align="center">Susceptibility Values for Tervalent Ions of Rare Earths</div>

Trivalent Ion	N_f	Ground State	p_B (theor.)			p_B (exper.)	
			g	H.	V.V.-F.		
La	0	$^1S_0$	$0/0$	0.00	0.00	diamag.	
Ce	1	$^2F_{5/2}$	$6/7$	2.54	2.56	2.41	2.5
Pr	2	$^3H_4$	$4/5$	3.58	3.62	3.5	3.6
Nd	3	$^4I_{9/2}$	$8/11$	3.62	3.68	3.5	3.7
Il	4	$^5I_4$	$3/5$	2.68	2.83	—	—
Sm	5	$^6H_{5/2}$	$2/7$	0.84	1.55	1.5	—
Eu	6	$^7F_0$	$0/0$	0.00	3.51	3.6	—
Gd	7	$^8S_{7/2}$	2	7.94	7.94	8.0	7.9
Tb	8	$^7F_6$	$3/2$	9.72	9.7	9.5	9.7
Dy	9	$^6H_{15/2}$	$4/3$	10.65	10.6	10.7	10.5
Ho	10	$^5I_8$	$5/4$	10.61	10.6	10.3	10.5
Er	11	$^4I_{15/2}$	$6/5$	9.58	9.6	9.5	9.6
Tu	12	$^3H_6$	$7/6$	7.56	7.6	7.3	7.3
Yb	13	$^2F_{7/2}$	$8/7$	4.54	4.5	4.5	4.5
Lu	14	$^1S_0$	$9/0$	0.00	0.00	diamag.	

The second column gives the number of electrons in the $4f$ shell, and the fourth column, values of g calculated by means of equation (12.11). Under p_B theoretical, the values deduced by Hund are given under H., while those derived by Miss A. Frank [2] using a relation derived by J. H. Van Vleck [3] (which is given below) are given under V. V.-F. Two sets of experimental values as derived by different investigators are given in the last two columns. [4] It will be observed that except in the case of samarium and europium, Hund's predictions are in agreement with the observed values.

In order to account for the discrepancy between theoretical and observed values in the case of europium and samarium it is necessary to note that Hund's equation (17.4) is based on the assumption that the energy difference between multiplets corresponding to different values of J is large compared to kT. Under these conditions it was necessary to consider only those orientations in a magnetic field which are due to that value of J corresponding to the lowest energy state of the multiplet levels. However, if the levels associated with

[1] F. Hund, *op. cit.*, p. 179, also in revised form in ref. E. C. S., p. 299 and ref. G. H., p. 209.

[2] *Phys. Rev.*, **39**, 119 (1932); **34**, 1494, 1625 (1929).

[3] J. H. Van Vleck, The Theory of Electric and Magnetic Susceptibilities, Chap. IX, The Clarendon Press, Oxford (1932).

[4] For references see ref. E. C. S.

different values of J are close together, so that the values of the *intervals*, $h\Delta\nu$, are *comparable with that of* kT, then there will be a considerable number of particles in each of the multiplet levels. As a consequence, the summation in equation (17.3) has to be extended over a larger number of states than those associated with the lowest value of J. The formula derived on this basis, by J. H. Van Vleck is quite complicated, but assumes relatively simple forms for two special cases.[1]

First, for values of $h\Delta\nu \ll kT$, the magnetic moment per atom in terms of μ_B is given by the relation,

$$p_B'' = \sqrt{L(L + 1) + 4S(S + 1)}, \qquad (17.9)$$

which applies only to free ions.

Second, the interaction between spin and orbital momentum may be completely removed by the interatomic field (which occurs in crystals). Then, the last equation reduces to the simple relation,

$$p_B''' =. \sqrt{4S(S + 1)}. \qquad (17.10a)$$

For n *unpaired* electrons, $S = n/2$. Hence the last equation may be written in the form [2]

$$p_B''' = \sqrt{n(n + 2)}. \qquad (17.10b)$$

By applying equation (17.9) it was possible, as shown in Table 17.1 to account for the discrepant results obtained for samarium and europium by means of Hund's relation.

In the case of divalent and tervalent ions of the second long series (from scandium to zinc) the relation deduced by Van Vleck leads to values of μ which are in much better agreement with observed values than those deduced by Hund's relation. As shown by Pauling,[3] equation (17.10b) yields, in general, results which are in good agreement with those observed for the case of ions of this series in solution, while the agreement in the case of crystalline compounds is not so good.

The existence of the crystalline field leads to a decrease with decrease in T of the "effective value" of the magnetic moment of the ion. Thus in the case of Sm^{3+} ions in solids it has been observed that μ eff. decreases from $1.55\mu_B$ at $T = 293°$ K to $1.06\mu_B$ at $74°$ K. As shown by A. Frank [4] the theory outlined above "can be applied only when the distortion by interatomic forces is negligible, that is, the energy to 'turn over' an ion against interatomic forces must be small compared to kT." The presence of this interatomic field causes a splitting up of the J levels in a manner which is analogous to that produced in "atomic energy" levels by magnetic fields (Zeeman effect).

[1] Ref. E. C. S., p. 313.

[2] This is the form used by ref. L. P., p. 106.

[3] *Op. cit.*, p. 107, which gives values of μ for the different ions.

[4] *Phys. Rev.*, **48**, 765 (1935).

Incidentally it is of interest to note that Pauling has used the observed values of μ for ions in solution and in solids as an aid in interpreting the nature of the bonds between atoms.

While equation (17.5) indicates that χ should increase as $1/T$, this law applies only at moderately high temperatures and for values of H that are not too high. For large values of H/T, that is, for strong fields and low temperature, χ tends to reach a saturation value. An interpretation of this observation and an equation which accounts for it quantitatively was first developed by L. Langevin on the basis of classical theory and a modified form was derived subsequently on the basis of quantum theory.[1]

When a magnetic field is applied to a paramagnetic or magnetic substance there is a rise in temperature (magneto-caloric effect), and conversely there is a cooling on removal of the field, which varies as $1/T$ and therefore becomes appreciable at temperatures near the absolute zero. This has been applied to produce temperatures below those obtainable by liquid helium.[2]

In conclusion it should be observed that on the basis of quantum mechanical considerations, W. Heisenberg, J. C. Slater and others have been able to deduce an interpretation of ferromagnetism.[3] While this theory is as yet able to account only approximately for some of the basic phenomena, it is a promising beginning towards a more intimate understanding of the extremely complex observations in this field.

18. Hyperfine Structure of Spectral Lines [4]

In previous sections it has been shown that the "fine" structure of many lines can be adequately interpreted as due to multiplet levels, to which are assigned quantum numbers L, S and J. Under extremely high resolving power the individual multiplet components are observed to possess a still finer structure, in which the interval between lines may be of the order of 2 cm.$^{-1}$ This splitting of a multiplet level into components which are extremely close to each other is known as *hyperfine structure (hfs)*.

Before proceeding to discuss the interpretation of these observations it is of interest to describe briefly certain refinements in spectroscopic technique which have made it possible to obtain the high resolution necessary for accurate determinations of wave lengths of *hfs* components.[5]

First of all, there is the improvement in gratings as a result of new techniques for ruling which R. W. Wood has introduced. Secondly, new sources

[1] J. H. Van Vleck, *op. cit.*, also ref. E. C. S.

[2] For discussion of the theory see ref. G. H., p. 210.

[3] For an elementary presentation the reader is referred to the paper by R. M. Bozorth, *Trans. Am. Inst. Elec. Engineers*, **54**, 1251 (1935); also ref. E. C. S., Chap. XI.

[4] *References:* H. E. W., Chap. XVIII; G. H., Chap. V; P. G., Chap. XI; A. C. C., Vol. 2, Chap. XX; H. Kallmann and H. Schueler, *Ergeb. exakt. Naturwiss.*, **11**, 134 (1932); H. A. Bethe and R. F. Bacher, *Rev. Mod. Phys.*, **8**, 206–225 (1936).

[5] These remarks are based on the discussion by A. G. Shenstone, *Reports on Progress in Physics*, **5**, 210 (1938).

have been developed for producing lines which are sufficiently fine for *hfs* analysis. The hollow-cathode tube originally used by Paschen for the excitation of spectra of gases and of low-melting-point metals was subsequently modified by H. Schueler and his collaborators into "the most powerful source of the excessively fine lines required in the examination of *hfs.*"

The most important factor in causing broadening of spectral lines is the Doppler effect, which arises from the random thermal motion of the atoms. It can be shown, on the basis of the kinetic theory of gases, that owing to this effect the half-value width of a line is equal to approximately $10^{-6}\lambda\sqrt{T/M}$, where M is the molecular or atomic weight of the radiating substance, and T, the absolute temperature. Hence, by cooling the discharge tube in liquid air, a considerable improvement is attained. However, still better results may be obtained, as shown by D. A. Jackson and H. Kuhn,[1] by application of the atomic beam method. The principle of this method, as described by these investigators, is as follows:

"If atoms evaporate from the surface of a liquid and then pass through a long cool tube so that any atom striking the wall of the tube is removed by condensation, then there will emerge from the further end of the tube an atomic beam in which all the atoms are moving in directions which differ only by very small angles from that of the axis of the cool tube. If d and l be the diameter and the length of the tube through which the atoms flow, then the greatest angle which the path of an atom can make with the axis of the tube is d/l, provided the number of atoms flowing through the tube is sufficiently small for there to be no collisions between atoms in the length of the tube. Now if these atoms are excited or allowed to absorb and the radiation or absorption is observed by means of a spectroscope the line of sight of which is at right angles to the direction of the atomic ray, then the Doppler width of the emitted or absorbed line will be smaller in the ratio of d to l than that of a line emitted by the atoms with their normal random distribution of velocities at the temperature of the liquid from which the atoms are evaporating. For the component of the mean velocity in the line of sight is only d/l of the total mean velocity. The width of the line is therefore equal to that given by a gas radiating or absorbing at a temperature of $(d/l)^2T$, T being the temperature of the liquid from which the atomic ray is evaporating. If, for example, the ratio of d to l is one to twenty the Doppler width of the emission or absorption line given by the atoms in the atomic beam is equal to that given by the atoms under normal gaseous conditions at a temperature four hundred times lower than that of the metal from which the atoms are evaporating. The atomic beam is therefore capable of giving lines which are very much narrower than could be obtained by working with a discharge tube cooled even to the temperature of liquid hydrogen."

R. Minkowski and H. Bruck[2] have shown by mathematical analysis that the shape of the line to be expected is not only quite different from that given by the usual Doppler formula, but also much narrower.

In the case of the red Cd line, $\lambda6438.5$, they obtained experimentally a width $\Delta\tilde{\nu} = 2.10^{-2}$ cm.$^{-1}$, corresponding to $\Delta\lambda = 8.3 \times 10^{-3}$ Å. Jackson and Kuhn applied the method to the measurement of *hfs* in absorption for the resonance lines of K, and observed a separation of about 1.5×10^{-2} cm.$^{-1}$ for the pairs of lines. Using a beam of sodium atoms, K. W. Meiszner and K. F.

[1] *Proc. Roy. Soc.*, [A], **148**, 335 (1935).

[2] *Z. Physik*, **95**, 274, 284 (1935).

Luft [1] have observed the *hfs* of the lines in emission with an accuracy of $\pm\, 5 \times 10^{-4}$ Å.

There are two causes which give rise to this type of structure: (*a*) the *isotope effect*, (*b*) *nuclear spin*.

(1) **Isotope Effect:** As mentioned previously, the Rydberg constant for any atomic species depends upon the nuclear mass in accordance with the relation

$$R = R_\infty \left(\frac{M}{M + m} \right), \tag{18.1}$$

where R_∞ is the Rydberg constant for infinite mass ($= 2\pi^2 m e^4 / ch^3$) and M and m denote the mass of nucleus and electron respectively.   Hence the frequencies of corresponding spectral lines should be slightly higher for the heavier of two isotopes.

The most important illustration of *hfs* of this type is that exhibited in the line spectrum of ordinary hydrogen, which is due to a mixture of the two isotopes $_1^1$H and $_1^2$H.   (It should be observed that the nuclear charge of an atomic species is indicated by a subscript at the lower left-hand corner, and the nuclear mass by the nearest integer, at *either* the upper left-hand corner or upper right-hand corner of the chemical symbol.)   In 1932 H. C. Urey, F. Brickwedde, and G. M. Murphy [2] showed that each of the Balmer lines has a very weak companion on the ultraviolet side which they interpreted as due to the presence of "heavy" hydrogen, $_1^2$H, which is customarily designated by the symbol, D (for deuterium).

The atomic masses of H and D, on the basis ^{16}O $= 16.00$, according to R. T. Birge [3] are 1.00813 and 2.01473 respectively.   Designating these atomic masses by m_H and m_D, the value of $\Delta\lambda$, according to equation (18.1), for corresponding lines (those having the same value of n in the Rydberg formula), should be given by

$$\begin{aligned}
\Delta(1/\lambda) &= -\,\Delta\lambda/\lambda^2 \\
&= \Delta R \left(\frac{1}{2^2} - \frac{1}{n^2} \right). \\
&= R_\infty \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \left(\frac{m_H - m}{m_H} - \frac{m_D - m}{m_D} \right).
\end{aligned}$$

Neglecting the difference between R_∞ and R_H this reduces to the relation,

$$\Delta\lambda = -\,\frac{\lambda m (m_D - m_H)}{m_H m_D} = -\,2.72 \times 10^{-4}\lambda.$$

Table 18.1 shows the wave lengths for the first four members of the Balmer

[1] *Ann. Physik,* **28,** 667 (1937); **29,** 698 (1937).

[2] *Phys. Rev.,* **40,** 1 (1932).

[3] Communication to author, August 1939; see also Appendix.

TABLE 18.1

	H_α	H_β	H_γ	H_δ
$\lambda(H)$	6562.79	4861.33	4340.47	4101.74 Å
$- \Delta\lambda$ obs.	1.79	1.33	1.19	1.12 Å
$- \Delta\lambda$ calc.	1.784	1.320	1.180	1.115 Å

series for H, the values of $- \Delta\lambda$ as calculated from the last equation, and for comparison the values of $- \Delta\lambda$ observed for the same line in the spectrum of D.

According to the best available data, the "abundance ratio" for H/D in water is normally about 6000, so that the lines due to D are extremely weak in the spectrum of ordinary hydrogen.

A fine structure due to the isotope effect has also been observed in the following elements: ^{6}Li and ^{7}Li; ^{20}Ne and ^{22}Ne; ^{64}Zn, ^{66}Zn and ^{68}Zn; Hg isotopes of mass 196, 198, 199, 200, 201, 202 and 204; ^{204}Pb, ^{206}Pb and ^{208}Pb; ^{203}Tl and ^{205}Tl. In all these cases, spectral terms due to heavier isotopes correspond to lower wave lengths than those due to lighter isotopes. For instance, for the ground term of Hg, the order of levels, starting with the *lowest* for ^{198}Hg, is 198, 200, 202 and 204. The term value for the last named isotope is 494×10^{-3} cm.$^{-1}$ less than for ^{198}Hg; that is, the electron is more tightly bound by the nucleus of lower mass.

According to G. Herzberg,[1] "A quantitative explanation of the isotope effect is not simple, since, with the exception of the H atom, it is not given merely by the altered Rydberg constant. A detailed, wave mechanical calculation shows that, for the lighter atoms (Li, Ne and so forth), an explanation can be obtained on the basis of different masses alone and is at least of the right order of magnitude. However, for the heavier elements, the effect is traced back to the *change of nuclear radius with mass.*"

(2) **Effect Due to Nuclear Spin:** Just as it has been found necessary to introduce the concept of electron spin to account for multiplet components observed under ordinary resolving powers, the suggestion [2] that the nucleus possesses an intrinsic angular momentum (with which is associated a magnetic moment) has led to an interpretation of a type of hyperfine structure which cannot be due to any isotope effect. For instance, elements which have only one isotope exhibit a hyperfine structure. Furthermore, the number and relative differences in values of λ for corresponding lines in different isotopes cannot be explained on the basis of a difference in mass alone.

It is assumed, therefore, that the nucleus possesses an angular momentum of magnitude $p = (h/2\pi)\sqrt{I(I + 1)}$ where I is a nuclear spin quantum number, which is a multiple of $\frac{1}{2}$. For the proton, $I = \frac{1}{2}$, and consequently this particle has the same angular momentum as the electron. In the case of the

---

[1] Ref. G. H., p. 185.

[2] W. Pauli, *Naturwiss.*, 12, 741 (1924). H. N. Russell also made the same suggestion independently.

electron, the associated magnetic moment, as mentioned previously, is

$$\mu_c = \frac{2e}{2mc} p = 2\mu_B \sqrt{s(s + 1)} = 1.73\mu_B,$$

where μ_B = Bohr magneton. On the same basis, we would expect for the nucleus of mass M, a magnetic moment of magnitude

$$\mu_I = \frac{2e}{2Mc} \cdot \frac{h}{2\pi} \sqrt{I(I + 1)}. \tag{18.2}$$

For the proton, $M = m_p = 1836.6m$, and $I = \tfrac{1}{2}$. Hence the corresponding nuclear moment should be

$$\mu_p = \frac{2\mu_B}{1837} \sqrt{I(I + 1)} \tag{18.3}$$

$$= 2\mu_s \sqrt{I(I + 1)}, \tag{18.4}$$

where μ_s is designated the *nuclear magneton.*

However, it has been found that the magnetic moments of the proton and of nuclei in general are greater than those indicated by equations (18.2) and (18.3). This is expressed formally by introducing the so-called *nuclear factor* g_I, and defining the nuclear magnetic moment by the relation *

$$\mu_N = g_I I \mu_s, \tag{18.5}$$

where

$$\mu_s = \mu_B/1837. \tag{18.6}$$

Since the values of g_I are of the order of unity, it follows that the values of μ_N are about 1000 times smaller than that of the electron.

In order to obtain the different *hfs* components of a spectral term, the procedure adopted is analogous to that used in deducing values of the vector J from those of the vectors L and S for ordinary spectral terms. The vector I is combined with the vector J to give a resultant designated by the quantum number F, and the *resultant total angular momentum of the atom as a whole, including nuclear spin,* is consequently given by the quantity $(h/2\pi)\sqrt{F(F + 1)}$. As in the case of LS coupling, F can assume the values:

$$F = J + I, \quad J + I - 1, \quad \cdots, \quad |J - I|. \tag{18.7}$$

For $J < I$, there are $2J + 1$ values of F running from $I + J$ to $I - J$, and for $J > I$, there are evidently $2I + 1$ values of F. Just as the interaction of the L and S vectors leads to a precession about the axis of the vector J, so

---

* The factor g_I may be determined, as indicated below, from the magnitude of the spacing between *hfs* components and a knowledge of the wave functions for the atom in the given state. Furthermore, what is determined experimentally in the case of deflection measurements in magnetic fields (see below) is the magnitude of $g_I = \mu_N/(I\mu_s)$. Hence μ_N gives the component of the magnetic moment in the direction of the field.

the interaction between the magnetic moments due to the nuclear vector I and that due to the electronic vector J leads to a precession about the axis of F as shown in Fig. 18.1.[1] This figure shows the precession of the vectors I and J about F for the component $F = 5$ of a $^5F_4$ term with $I = 2$. In this case $S = 2, L = 3$ and $J = 4$. The relatively faster precession of L and S about J is shown by the dotted-line ellipse, and the very slow precession of J and I about F is shown by the solid-line ellipse. The interaction in each case is proportional to the cosine of the angle between the two vectors and thus leads to a difference in energy for two states associated with different values of J or F. Only, since the nuclear magnetic moment is considerably less than that of the electron, the energy differences are also very much less in the case of *hfs* components.

Fig. 18.1. Precession of the Angular Momentum Vectors About the Total Angular Momentum F for the Component $F = 5$ of a $^5F_4$ Term with $I = 2$

The same selection rule applies to F as to J. That is,

$$\Delta F = \pm 1, \quad \text{or} \quad 0,$$
$$F = 0 \text{ to } F = 0 \text{ is forbidden.}$$

Also a similar rule applies for the relative magnitudes of the intervals between different *hfs* components of a spectral term. The interaction energy is evaluated in the same manner as that for LS coupling[2] by means of the relation

$$\Gamma_F = \tfrac{1}{2}A'\{F(F + 1) - I(I + 1) - J(J + 1)\}, \tag{18.8}[3]$$

where A' is a constant of the same nature as a in equation (15.16) and A in equation (15.18).

Figure 18.2[4] shows the application of this rule to a $^2D_{5/2}$ level where $I = 9/2$. In this case, $J = 5/2$, and the resultant values obtained by the interaction of the J and I vectors, as shown in the diagram at the extreme right, are $F = 7, 6, 5, 4, 3$ and 2. The relative values of Γ_F, as calculated by equation (18.8), are shown for each value of F, and the successive intervals, as will be noted, are in the ratio of the larger F values. For the two levels F and $F - 1$ the interval is

$$\Delta\Gamma_F = \frac{A'}{2} \{F(F + 1) - (F - 1)F\} = A'F.$$

The application of the interval rule as well as that of the selection principle for F are illustrated in Fig. 18.3[5] which shows the *hfs* structure of the line
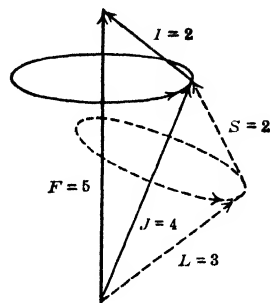
[1] Ref. G. H., p. 188.
[2] See equation (15.16).
[3] For further details see Bethe and Bacher, *loc. cit.*
[4] Ref. H. E. W., p. 355.
[5] Ref. P. G., p. 213; ref. H. E. W., p. 357.

$\lambda 4722$ in bismuth, corresponding to the transition $6p^27s(^2S_{1/2}){\to}6p^3(D^1{}_{3/2})$. It should be observed that in this case the lower levels are "inverted." Furthermore, the fine structure in Bi exhibits jj—rather than LS—coupling; hence it is possible to have the transition from a ^2S to a ^2D term. For the bismuth nucleus, $I = \tfrac{9}{2}$, and as seen in Fig. 18.3, while the interval rule is obeyed only approximately, the number of components is in accordance with the selection rule stated above.

Figure 18.4 [1] shows a photometer curve for the *hfs* components of this line and of the spectral wave length region over which these extend. The relative intensities, which are indicated at the bottom, are in good agreement with those calculated from the equations for multiplet components if J, L and S in these equations are replaced by F, J and I respectively.

Fɪɢ. 18.2. Vector Diagram Illustrating Graphically the Interval Rule for Hyperfine Structure. Specific example of a $^2D_{\frac{3}{2}}$ level where $I = 9/2$.
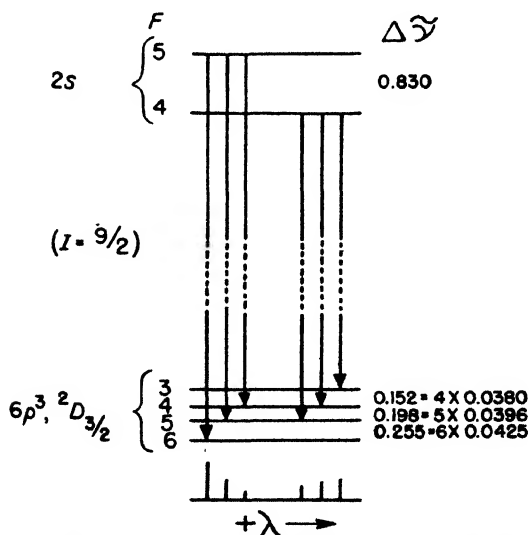
Fɪɢ. 18.3.   Illustrating Selection and Interval Rule for *hfs* of λ 4722 in Bismuth

[1] Ref. P. G., p. 213.

In a magnetic field, a space quantization of F occurs, exactly as in the case of J for ordinary multiplet components of a term. A magnetic quantum number M_F has to be introduced which is analogous to M. Thus

$$M_F = F, \quad F - 1, \cdots, -F, \quad (18.9)$$

and there are $2F + 1$ states associated with the state F. The Landé g-factor for the Zeeman effect is deduced for *hfs* components by a relation similar to that given in equation (12.11), except that J, L and S in the latter are again replaced, as in the case of the equations for relative intensities, by F, J and I respectively. However, as Herzberg points out,[1] "In actual investigations, the Zeeman effect is scarcely ever observed, since the hyperfine structure splitting itself is generally close to the limit of possible resolution."

In strong fields, the Paschen-Back effect is observed, as in the case of ordinary multiplet terms. Owing to the extremely weak coupling between

FIG. 18.4. Photometer Curve for *hfs* Components in Fig. 18.3 Showing Relative Intensities of the Six Components

J and I, this effect is obtained at much lower field strengths than for ordinary multiplet components.[2] The magnetic field destroys the interaction between I and J and the resulting space quantization can be interpreted in terms of the two quantum numbers M_J and M_I, where

$$M_J = M = J, \quad J - 1, \quad \cdots, \quad -J$$

and

$$M_I = I, \quad I - 1, \quad \cdots, \quad -I.$$

Thus, in a strong field, each term in a multiplet is split up into $2I + 1$ components, whereas in absence of nuclear spin the number of components would be $2J + 1$. Table 18.2 shows the changes in splitting up produced in a term with $J = \frac{1}{2}$, $I = \frac{3}{2}$ as the magnetic field is increased. It will be observed that the total number of components remains the same for both weak and strong fields, as in the case of ordinary multiplets, but in strong fields they are located symmetrically in two groups, each associated with a value of M and containing $2I + 1 = 4$ components. Thus by counting the total number of components in a magnetic field, the value of I can be derived.

[1] Ref. G. H., p. 192.

[2] Usually designated as the Back-Goudsmit effect in *hfs*. See ref. H. E. W., p. 376.

TABLE 18.2

Weak Fields		Strong Fields	
$F = I + J$	M_F	M_I	$M_J = M_F - M_I$
2	$+2$	$+\frac{3}{2}$	$+\frac{1}{2}$
	$+1$	$+\frac{1}{2}$	
	0	$-\frac{1}{2}$	
	-1	$-\frac{3}{2}$	
	-2	$-\frac{3}{2}$	$-\frac{1}{2}$
1	-1	$-\frac{1}{2}$	
	0	$+\frac{1}{2}$	
	$+1$	$+\frac{3}{2}$	

It follows that the *total statistical weight* of a term with a given value of J is

$$(2J + 1)(2I + 1),$$

if nuclear spin is included. However, since the factor $2I + 1$ is the same for all states of an atom, this result does not affect the calculation of relative intensities as described in a previous section.

(3) **Determinations of I, g and μ for Nuclei:** [1] One method for the determrniation of I has been indicated above; another method is as follows. Usually the J values are known. If now the terms of a hypermultiplet can be arranged in a square array in such a manner that corresponding values of F are determined, then, in accordance with equation (18.7), the value of I is also determined. From the observed values of the wave number intervals between *hfs* components it is then possible by means of equation (18.8) to calculate g_I in a number of cases for which the exact form of the function A' is known. Expressions for this function, which are similar to those for the separation of ordinary multiplet components, have been derived on the basis of wave mechanics, by S. A. Goudsmit [2] and E. Fermi and E. Segrè. [3] Since $\mu_N = \mu_s g_I I$, it is thus possible to derive a value of μ_N. [4]

The nuclear spin may be determined from the number of components observed in the Zeeman effect, as described above.

Observations on the relative intensities of lines in band spectra have also been used. The theory of this method is described by Bethe and Bacher [3] as

[1] Besides the references given above, the discussion on "Nuclear Moments" by H. A. Bethe and R. F. Bacher, *Rev. Mod. Phys.*, **8**, 206 (1936) should be consulted.

[2] *Phys. Rev.*, **44**, 636 (1933).

[3] *Z. Physik*, **82**, 729 (1933). See also discussion of these formulae by H. A. Bethe and R. F. Bacher, *loc. cit.*

[4] For an illustration of the application of this method see the publication by R. A. Fisher and E. R. Peck, *Phys. Rev.*, **55**, 270 (1939) on the determination of g and μ for Mn, also T. Schmidt, *Z. Physik*, **108**, 408 (1938).

[5] *Loc. cit.*, p. 207. The quantitative formulae are given on p. 214.

follows: "For diatomic molecules composed of like atoms it is found that the presence of nuclear angular momentum changes the statistical weight of the rotational states. For zero nuclear angular momentum we find that alternate lines of the bands are missing. With a nuclear angular momentum it is found that successive lines of the bands have an intensity ratio which depends on the magnitude of the nuclear spin. It is thus possible by studying the intensities in such molecular spectra to determine the nuclear angular momentum."

However, the most direct methods for the determination of nuclear magnetic moments are those involving the deflection of atomic beams in magnetic fields. As mentioned in Section 12(3) such a method was originally devised by Stern and Gerlach for the determination of magnetic moments of atoms, and the principle has been applied directly by R. Frisch, I. Estermann and O. Stern [1] to determine the magnetic moment of the proton, for which the spin quantum number is $\frac{1}{2}$. A beam of hydrogen molecules is passed through a strong magnetic field which has a steep gradient at right angles to the direction of the beam. The magnetic moment of the atom is determined from the amount of splitting of the beam by the field. Now ordinary hydrogen consists of 3 parts ortho- and 1 part para-hydrogen. In the former, the nuclear spins are in the same direction, and in the latter, in opposite directions. Hence for pure parahydrogen (which is the stable form of H_2 at liquid air temperatures) any observed magnetic field splitting is due to the rotational momentum of the molecule. On the other hand, orthohydrogen splits into three components (correspond to the total spin 1), and from the observations on parahydrogen it is possible to introduce a correction for the rotational spin of the molecule. In this manner Stern and his associates were able to derive a preliminary value of $\mu_P = 2.5\mu_s$.

Subsequently I. Estermann and O. Stern [2] obtained by application of the same method, for the magnetic moment of the deuteron (the nucleus of $^2_1\mathrm{H}$), a value $\mu_D = 0.5$ to $1.0\mu_s$. From measurements of relative intensities of lines in the molecular spectrum of deuterium G. M. Murphy and H. Johnston [3] deduced for the nuclear spin of the atom the value $I = 1$.

More accurate values of μ_P and μ_D were obtained by I. I. Rabi, J. B. Kellogg and J. R. Zacharias [4] in 1934 by deflecting a beam of neutral hydrogen or deuterium atoms by a weak magnetic field of extremely high gradient. In this weak field "the nuclear spin is only partially decoupled from the electron spin, and the nuclear moment can be evaluated by measuring the atomic magnetic moments of the magnetic levels." Since the hydrogen atoms are in state $^2S_{1/2}(J = \frac{1}{2})$ and the nuclear spin is $\frac{1}{2}$, the number of magnetic levels is $(2J + 1)(2I + 1) = 4$. The relative spacing of the levels depends, as in the Zeeman effect, upon the magnitude of the nuclear moment.

A radically new method of measuring magnetic moments of nuclei was

[1] Z. Physik, **85**, 4, 17 (1933).
[2] Phys. Rev., **45**, 761 (1934).
[3] Ibid., **46**, 95 (1934).
[4] Ibid., **46**, 157, 163 (1934); see also, ibid., **50**, 472 (1936).

described by I. Rabi and his associates [1] in 1939. In this "molecular beam resonance method," as it has been designated, the arrangement used may be described briefly as follows: [2] The beam of atoms is sent first through one inhomogeneous field at right angles to the direction of the beam and then through another field of oppositely directed gradient. Both fields are of equal magnitude. "A molecular beam of the substance to be studied possesses a sigmoid path in these magnets and is focused on a suitable detector. A third magnet which produces a homogeneous field is placed in the region between the two deflecting magnets. In this strong homogeneous field the nuclear moments are decoupled from other nuclear moments and from rotational moments of a molecule in a $^1\Sigma$ state, and precess with their Larmor frequency,

$$\nu = \frac{\mu H_0}{hI} \cdot \tag{18.10}$$

"An oscillating field perpendicular to the homogeneous field produces transitions to other states of space quantization when the frequency of this field is close to ν. If such transitions take place the molecule is no longer focussed on to the detector by the subsequent inhomogeneous field and the observed intensity diminishes." Thus the value of ν given by equation (18.10) is determined by varying the frequency of the oscillating circuit until minimum intensity is observed on the detector—hence the designation of resonance method. [3]

Utilizing this method as well as the earlier magnetic beam method, Rabi and his associates have obtained significant results on the *hfs* of a number of nuclei and the values of the nuclear magnetic moments. [4]

Table 18.3 [5] gives values of I and μ_N, expressed in terms of μ_s, the nuclear magneton, as obtained by application of the resonance method, also a few other values taken from the tables published by H. A. Bethe and R. F. Bacher. [6]

While the discussion of nuclear structures is beyond the scope of this chapter, it is obvious that determinations of μ_N must be of great significance in connection with any theory of nuclear structure. On the basis of the theory

[1] I. I. Rabi, S. Millman, P. Kusch and J. R. Zacharias, *Phys. Rev.*, **55**, 526 (1939).

[2] This method is in a sense an elaboration of the procedure used by I. I. Rabi and W. W. Cohen (*Phys. Rev.*, **43**, 582 (1937)) for measuring the nuclear spin of sodium. The $(2J + 1)$ levels were obtained in this case by passing the beam of atoms first through a field which decoupled nuclear and electronic spins, screening off all but one of these beams, and then splitting up the residual beam by a second relatively weak field into $(2I + 1)$ components.

[3] See S. Millman, *Phys. Rev.*, **55**, 628 (1939) for discussion of the method used for determining the sign of μ_N.

[4] See references to Table 18.3, also the following more recent papers:

N. A. Renzetti, *Phys. Rev.*, **57**, 753 (1940); ^{69}Ga and ^{71}Ga.

P. Kusch, S. Millman and I. I. Rabi, *ibid.*, **57**, 765 (1940); ^{6}Li, ^{7}Li, ^{39}K and ^{41}K.

S. Millman and P. Kusch, *ibid.*, **58**, 438 (1940); ^{23}Na, ^{85}Rb, ^{87}Rb and ^{133}Cs.

[5] A table of values of μ_N and I with references to original papers has also been published by T. Schmidt, *Z. Physik*, **108**, 408 (1938).

[6] *Loc. cit.*, p. 216.

TABLE 18.3 [1]

Atom	Z	I	μ_N	Reference
^{1}H.............	1	½	2.785 ± 0.02	1
^{2}H(D)	1	1	0.855 ± 0.006	1
^{6}Li......... ...	3	1	0.820	2
^{7}Li...........	3	3⁄2	3.250	2
Be.......... .	4	?	Negative	8
^{10}B.........	5	1	0.597	3
^{11}B...........	5	3⁄2	2.682	3
^{11}C....	6	3⁄2	− 1.65	9
^{13}C...........	6	½	1.13	9, 10
^{13}N........ .	7	½	− 0.75	9
^{14}N...........	7	1	0.402	4
^{19}F........ .	9	½	2.622	2
^{23}Na.........	11	3⁄2	2.216	4
^{27}Al........	13	5⁄2	3.628	5
^{35}Cl...........	17	5⁄2	1.365	6
^{39}K...... ...	19	3⁄2	0.391	4
^{83}Kr......... .	36	9⁄2	− 1	B. B.
^{85}Rb....... .	37	5⁄2	1.345	6
^{87}Rb...........	37	3⁄2	2.741	6
^{113}Cd...........	48	½	− 0.65	B. B.
^{115}In..........	49	9⁄2	6.40	7
^{133}Cs........	55	7⁄2	2.572	4
^{199}Hg.........	80	½	0.5	B. B.
^{201}Hg...... ..	80	3⁄2	− 0.6	B. B.
^{203}Tl....... ..	81	½	1.4	B. B.
^{205}Tl....... ..	81	½	1.4	B. B.
^{207}Pb........ .	82	½	0.6	B. B.
^{209}Bi...........	83	9⁄2	4.0	B. B.

[1] *References to Table* 18.3:

1. J. M. B. Kellogg, I. I. Rabi, N. F. Ramsey, Jr., and J. R. Zacharias, *Phys. Rev.*, **56**, 728 (1939).
2. I. I. Rabi, S. Millman, P. Kusch and J. R. Zacharias, *ibid.*, **55**, 526 (1939).
3. S. Millman, P. Kusch and I. I. Rabi, *ibid.*, **56**, 165 (1939).
4. P. Kusch, S. Millman and I. I. Rabi, *ibid.*, **55**, 1176 (1939).
5. S. Millman and P. Kusch, *ibid.*, **56**, 303 (1939).
6. P. Kusch and S. Millman, *ibid.*, **56**, 527 (1939).
7. S. Millman, I. I. Rabi and J. R. Zacharias, *ibid.*, **53**, 384 (1938).
8. P. Kusch, S. Millman, I. I. Rabi, *ibid.*, **55**, 666 (1939).   Assuming $I = \frac{1}{2}$, $\mu_N = -0.392$; for $I = \frac{3}{2}$, $\mu_N = -1.175$.
9. M. E. Rose and H. A. Bethe, *ibid.*, **51**, 205 (1937).
10. D. R. Inglis, *ibid.*, **58**, 577 (1940).

In a paper by S. Millman and P. Kusch, *Phys. Rev.*, **60**, 91 (1941), more recent precision measurements are given for many of the nuclei mentioned in the table.

that nuclei are composed of neutrons and protons, table 18.4 gives the structures and values of μ_N for a few of the lighter nuclei, where p denotes the proton, n, the neutron, and α, the alpha particle.

TABLE 18.4

Nucleus	Structure	μ_N	I	$\Delta\mu_N$
^{1}H............	p	2.785	$\frac{1}{2}$	
^{2}H(D)	np	0.855	1	-1.93
^{6}Li...........	αnp	0.820	1	
^{7}Li..........	αnpm	3.250	$\frac{3}{2}$	$+2.43$
^{10}B....	$2\alpha np$	0.597	1	
^{11}B....	$2\alpha npm$	2.682	$\frac{3}{2}$	$+2.085$

The neutron, like the proton, possesses a half-integer spin, which accounts for the increase of $\frac{1}{2}$ in the value of I on addition of a neutron. However, in the case of Li and B, the addition of a neutron increases μ_N, while in case of D with respect to H, $\Delta\mu = -2$ approximately. The ratio μ_D/μ_P is equal to 3.28 from the data given above, whereas from measurements of the velocity of conversion of ortho- into para-hydrogen, Farkas and Farkas [1] derived a value of 4.

The following remarks upon the relation between magnetic moments of nuclei and structures are taken from the review on hyperfine structure by M. F. Crawford.[2]

"Recently," he writes, "a rational theory of nuclear moments has been developed for light nuclei [3] (mass number between 6 and 16), using the individual particle model (Hartree model). By assigning quantum states and individual wave functions to each nuclear particle, one can calculate, in the same manner as for atomic spectra, the energy of the various terms which arise from any given configuration of neutrons and protons. The important feature for nuclear moments is to predict which of the spectroscopic states of the nucleus will be most stable. The nuclear magnetic moment can then be calculated from considerations as to the coupling of the spin and orbital momenta of the nucleus in the ground state. The calculations involve the same specific nuclear forces as are used in other phases of nuclear physics, and assume that the magnetic moments of the proton and neutron are not modified by the nuclear binding process. Thus the moments are predicted without any empirical adjustment of parameters."

On the basis of these quantum mechanical considerations it has thus been found possible to account for the observed difference in the values of μ_N for ^{6}Li and ^{7}Li, and for ^{10}B and ^{11}B respectively [4] and for other relations between values of μ_N for different nuclei.

The presence of negative magnetic moments is another fact of interest in any such theory of binding between neutrons and protons. Bethe and Bacher have pointed out certain relations between values of μ and the structure, but a more explicit theory of the nature of the forces between the two elementary particles is required before it will be possible to account quantitatively for

[1] *Proc. Roy. Soc.*, [A], 152, 152 (1935).

[2] *Reports on Progress in Physics*, 5, 227 (1938).

[3] E. Feenberg and E. Wigner, *Phys. Rev.*, 51, 95 (1937); M. E. Rose and H. A. Bethe, *ibid.*, 51, 205 (1937); D. R. Inglis, *ibid.*, 53, 470, 880 (1938).

[4] M. E. Rose and H. A. Bethe, *loc. cit.*

the observed values of nuclear moments. Furthermore, more accurate experimental values are necessary in many cases, since those available at present are based on more indirect methods, such as the investigations of intensities of lines in band spectra.

19. QUANTUM THEORY OF VALENCE [1]

(1) **Types of Bonds:** The chemist distinguishes different types of bonds. There is, first, the *covalent* bond, such as exists between the two atoms in H_2, or between C and H in CH_4, etc. The Lewis-Langmuir theory interprets this bond as involving the sharing of a pair of electrons by the two bonded atoms, which is designated by writing the molecular formulae in the forms,

$$\text{H:H;} \quad \text{H:}\overset{..}{\underset{..}{C}}\text{:H,} \quad \text{and so forth.}$$

with H above and below the central C.
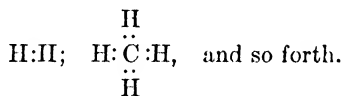
Similarly double and triple bonds are represented by four and six shared electrons respectively, as in the formulae

$$\overset{H}{\underset{H}{}} \!:\! C :: C \!:\! \overset{H}{\underset{H}{}}, \quad \text{and} \quad H : C ::: C : H.$$
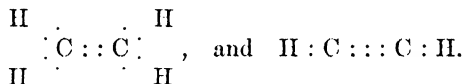
Secondly, we have the *ionic* bond, which results from the electrostatic attraction between two atoms or groups of atoms of opposite charges. A typical illustration is furnished by NaCl, which is ionized in solution and whose crystal lattice is constituted of Na^+ and Cl^- ions at opposite corners of a cube. Each sodium ion is held by the attraction of the six oppositely charged chlorine ions which are its nearest neighbors, and similarly each chlorine ion is held by six neighboring sodium ions. NaCl is often designated a *polar* compound, while H_2, CH_4, etc., are known as *homopolar* compounds. As will be pointed out below, most compounds are neither purely polar nor purely homopolar, but represent transitions between these two types of bonding. In virtue of this, the binding energy is greater than it would be for a single type of bonding.

In covalent compounds such as benzene, for which the organic chemist has postulated two or more different possible types of linkage of atoms, quantum mechanics has shown that there is an additional energy of binding, due to this possibility of interchange of electrons. This is known as *resonance energy*.

The energy of binding of two hydrogen atoms cannot be accounted for quantitatively on the basis of any simple classical model for which the total energy is deduced from the sum of the energy of attraction between nuclei and

[1] *References:* W. G. Penney, The Quantum Theory of Valency, Methuen and Co., London, England (1935) (Ref. W. G. P.); J. H. Van Vleck and A. Sherman, The Quantum Theory of Valence, *Rev. Mod. Phys.*, **7**, 167 (1935) (Ref. V. V. S.); L. P., *op. cit.*; G. H., *op. cit.*; S. D., *op. cit.*

electrons and that of repulsion between particles of similar charge. As will be shown in the following section, such a calculation yields a value for the binding energy which is less than ten percent of that actually observed. A successful solution of this problem was first derived, on the basis of wave mechanics, by W. Heitler and F. London.[1] We shall therefore review this theory in the following section.

(2) **The Heitler-London Theory of the Hydrogen Molecule:** Let us consider the system consisting of two protons A and B and two electrons (see Fig. 19.1). If the two atoms are completely separated, the energy of the system (zeroth order energy) is $2E_0$, where E_0 is the energy of the hydrogen atom in the normal

state. If electron (1) is attached to uuclens A and electron (2) to nucleus B, the so-called zeroth order eigenfunction for the two atoms (compare the treatment of the helium atom problem) is $\psi(1)\phi(2)$, where

$$\psi(1) = \sqrt{\frac{1}{\pi a_0{}^3}}\, e^{-r_{A1}/a_0}, \quad (19.1)$$

$$\phi(2) = \sqrt{\frac{1}{\pi a_0{}^3}}\, e^{-r_{B2}/a_0}, \quad (19.2)$$

where a_0 = radius of Bohr orbit, and r_{A1} and r_{B2} are the distances shown in Fig. 19.1.
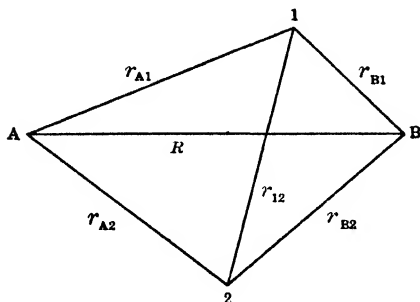
FIG. 19.1. Illustrating Notation Used in Discussing Theory of Formation of Hydrogen Molecule. The nuclei of the atoms are designated by A and B, the two electrons by 1 and 2

But *we may interchange the electrons* and obtain for the *same* zeroth order energy an eigenfunction of the form $\psi(2)\phi(1)$, where r_{A2} replaces r_{A1} in (19.1) and r_{B1} replaces r_{B2} in (19.2). The system is therefore *degenerate*, in the same manner as the excited state of the helium atom, and as in the latter problem it is found that the correct zeroth order eigenfunctions for the system must be the two functions,

$$\phi_\alpha{}^0 = \frac{1}{\sqrt{2 + 2S^2}}\{\psi(1)\phi(2) + \psi(2)\phi(1)\} \quad (19.3)$$

and

$$\phi_\beta{}^0 = \frac{1}{\sqrt{2 - 2S^2}}\{\psi(1)\phi(2) - \psi(2)\phi(1)\}. \quad (19.4)$$

Evidently $\phi_\alpha{}^0$ is a *symmetric* function, since interchange of coordinates does not change the sign of the expression, while $\phi_\beta{}^0$ is *antisymmetric*. In these equations S is a function of $\rho = R/a_0$, of the form

$$S = e^{-\rho}(1 + \rho + \tfrac{1}{3}\rho^2). \quad (19.5)$$

[1] *Z. Physik*, **44**, 455 (1927).

When the atoms are at a distance from each other, ρ is very large, and consequently S is negligible. There is no interchange of electrons. But as ρ decreases, the frequency of interchange of electrons increases and its magnitude is given by η/h, where η is the interaction energy resulting from the coupling of atoms A and B. Fig. 19.2 shows a plot of S^2 as a function of ρ.[1]
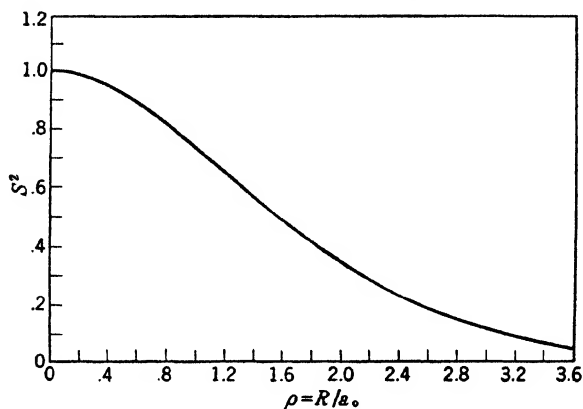
FIG. 19.2. Plot of S^2 as a Function of Internuclear Distance

Calculation, on the basis of wave mechanics, shows that the interaction energy is given for the symmetrical case by an expression of the form,

$$\eta_\alpha = \frac{E_{11} + E_{12}}{1 + S^2}, \qquad (19.6)$$

and for the antisymmetrical case, by

$$\eta_\beta = \frac{E_{11} - E_{12}}{1 - S^2}, \qquad (19.7)$$

where E_{11} represents the coulomb interaction of the electric charge distributions, and E_{12} corresponds to the *exchange* or *resonance energy* which arises from the possibility of interchange of electrons.

Thus the quantum mechanics treatment of the problem leads to the conclusion that two hydrogen atoms *can interact in two different modes*, and the fundamental reason for this is the fact that the two electrons are absolutely equivalent, so that it is impossible to distinguish between them. On the basis of classical considerations the total interaction energy would be E_{11}. Quantum mechanical considerations lead to the introduction of the term $\pm E_{12}$. Evidently both E_{11} and E_{12} are functions of ρ, and Fig. 19.3 [2] shows the results

[1] Ref. S. D., p. 322.
[2] Ref. S. D., p. 315.

deduced by J. Sugiura,[1] which are more accurate than those derived previously by Heitler and London. The values of η_α (curve S) and η_β (curve A) are given in electron-volts,[*] as functions of the internuclear distance. It will be observed that for values of $R/a_0 > 1$, η_α is negative (indicating *binding* energy) and reaches a minimum value of -3.2 electron volts for $R = 1.52a_0$, that is, $r = 0.80 \times 10^{-8}$ cm. On the other hand, η_β is positive. Thus, η_α represents the lower energy state and *must correspond to molecule formation*, while η_β must represent a *repulsive energy* between the two atoms. Consequently, the symmetric function $\phi_\alpha{}^0$ represents a *stable state*, while the antisymmetric function, $\phi_\beta{}^0$ represents an unstable state.

FIG. 19.3. Energy as Function of Internuclear Distance for the Two Modes of Interaction of Two Hydrogen Atoms; Curve S Corresponds to the Symmetric, and Curve A to the Anti-Symmetric Mode

Figure 19.4 [2] shows plots of the functions E_{11}, E_{12}, $E_{11} + E_{12}$ and $E_{11} - E_{12}$ in terms of kilocalories per mole. For comparison there is also plotted the potential energy curve deduced by P. M. Morse [3] from observations on the band spectrum of H_2. According to H. Beutler [4] the energy of dissociation as deduced from the band spectrum (that is, the minimum value of E) is 108,900 cal./mole, that is, 4.72 volts, and the corresponding value of R, the internuclear distance, is 0.749×10^{-8} cm.

As shown in Fig. 19.4, E_{12} is *negative* (over a large range of values of R/a_0) and represents a considerably greater binding energy than E_{11}. Furthermore, for all values of $R/a_0 > 1$, S^2, as shown in Fig. 19.2 is less than 1. Hence for $R/a > 1$, $E_{11} + E_{12}$ is negative and $E_{11} - E_{12}$ is positive. Actual evaluation of the expression for E_{11} shows that this has a minimum value of -0.488 volt for $R = 1.90a_0$. Since the corresponding value of S^2 is 0.347, it follows that $-E_{11}/(1 + S^2) = 0.362$ volts $= 8350$ cal./mole, which is about 11.3 per cent of the theoretical value calculated on the basis of the Heitler-London theory, and about 7.7 per cent of the total observed binding energy.

[1] *Z. Physik*, **45**, 484 (1927).

[*] 1 e.v. = 23.055 kcal./mole.

[2] S. D., *op. cit.*, p. 316.

[3] *Phys. Rev.*, **34**, 57 (1929); E. U. Condon and P. M. Morse, Quantum Mechanics, McGraw-Hill Book Co. (1929). This curve is also discussed by S. D., *op. cit.*, Chap. XIII. As shown by Morse, the potential energy E, as a function of $\rho = R/a_0$, maybe represented very satisfactorily by an expression of the form,

$$E(\rho) = -2E_0 e^{-\beta\rho} + E_0 e^{-2\beta\rho},$$

where E_0 is the value at the minimum on the curve shown in the figure, and β is a constant the value of which depends upon the mass of the molecule and vibration frequency of the bond.

[4] *Z. physik. Chem.* [B], **27**, 287 (1934); **29**, 315 (1935).

"If there were no possibility of interchange of electrons between the two atoms, the total binding energy would be given by the minimum value of E_{11} alone, . . . which corresponds to. the interaction energy of the nuclei and electron charge distributions for each electron about their respective nuclei. However, as the atoms are made to approach there is an increase in the frequency of interchange of electrons, and this is taken into account by the *exchange integral* (E_{12})."
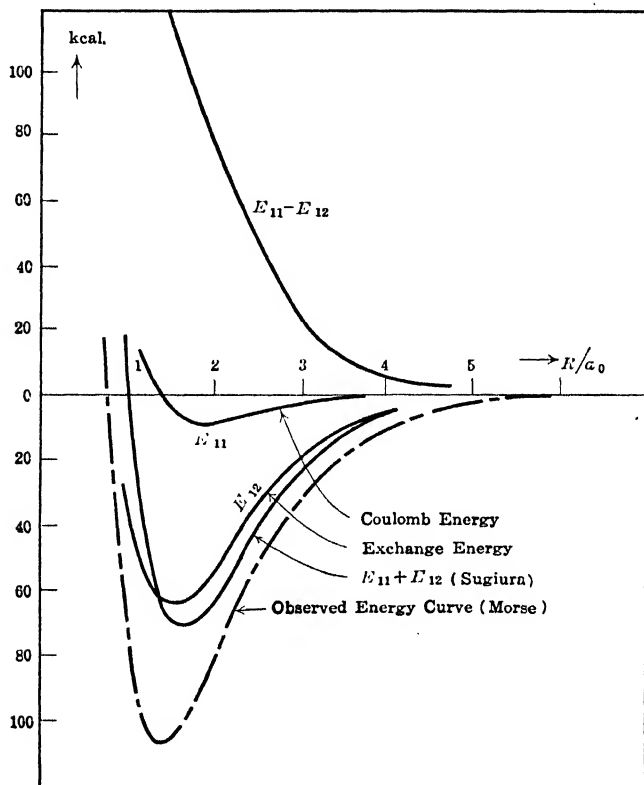
Fig. 19.4. Plots of the Total Energy, Coulomb Energy and Exchange Energy as Functions of Internuclear Distance, for the Two Modes of Interaction of Two Hydrogen Atoms

"A great deal has been written about the non-classical nature of the term E_{12}, and since this term accounts, as shown above, for a large part of the energy of formation of H_2, a distinction has been drawn between the types of forces involved in the two energy terms. Evidently such a distinction is only the result of the mathematical computation, for, as a matter of fact, the quantum-mechanical treatment recognizes that the only forces involved in the binding of two hydrogen atoms are those which arise from electrostatic attraction and repulsion between the four particles which constitute the system. The exchange integral is merely an expression of the physical requirement that the electrons in H_2 cannot be regarded as localized about the nuclei with which they were associated in the separated atoms." [1]

[1] S. Dushman and F. Seitz, *J. Phys. Chem.*, **41**, 233 (1937).

In the following section the reason will be discussed for the discrepancy between the value of the binding energy deduced by the Heitler-London method and that observed experimentally. While this indicates that this treatment is incomplete, the very fact that the term E_{12} accounts for a large fraction of the observed binding energy leads to the identification of the energy E_{12} with that of the valence bond. We thus obtain a quantitative interpretation of the shared-electron bond postulated by Lewis and Langmuir.
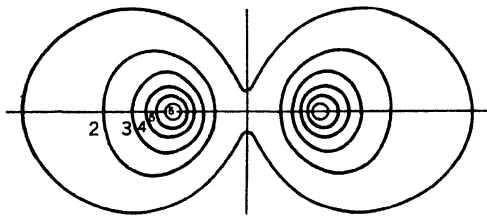
FIG. 19.5.   Electron Distribution for Elastic Reflection of Two Hydrogen Atoms

This is made even more evident from the plots of $(\phi_\alpha{}^0)^2$ and $(\phi_\beta{}^0)^2$, which correspond to the *densities of charge distribution* for the two curves S and A, respectively, shown in Figs. 19.5 and 19.6.[1] These represent plots of the two functions in two dimensions. The density is constant for each curve and the numbers attached give the relative densities or probabilities of occurrence of the electrons. Fig. 19.5, corresponding to curve A, illustrates the elastic reflection which occurs when the two hydrogen atoms collide without molecule formation. It will be observed that in this case the charge density is greatest for regions removed from the center of the line joining the two nuclei. On the other hand, Fig. 19.6, which corresponds to curve S, and represents the distribution for molecule formation (*homopolar combination*), shows that in this case the electrons tend to occur for a large part of the time, in the region between the nuclei.

FIG. 19.6.   Electron Distribution for Hydrogen Molecule Formation

"As in the case of the helium atom we must take into account *electron spin*. Let us designate the two spin functions $\psi(\frac{1}{2})$ and $\psi(-\frac{1}{2})$ by α and β respectively. Then the only completely *antisymmetrical functions* which can be obtained from the space functions $\phi_\alpha{}^0$ and $\phi_\beta{}^0$ are the following:

$$\phi_\alpha{}^0\{\alpha(1)\beta(2) - \alpha(2)\beta(1)\}; \quad (\Sigma m_s = 0),$$
$$\phi_\beta{}^0\{\alpha(1)\beta(2) + \alpha(2)\beta(1)\}; \quad (\Sigma m_s = 0),$$
$$\phi_\beta{}^0\alpha(1)\alpha(2) \text{ and } \phi_\beta{}^0\beta(1)\beta(2); \quad (\Sigma m_s = \pm 1).$$

[1] F. London, *Leipziger Vorträge*, 1928, pp. 59–84.

"Since only the first of these involves $\phi_\alpha{}^0$ and the other three involve $\phi_\beta{}^0$, it is concluded that molecule formation occurs only when the *spins are anti-parallel*. On the other hand, elastic reflection occurs when the spins are parallel, and the resulting total spin can then have the values $+1$, 0 and -1.

"Thus we find that there exist three possible states in which the atoms repel each other and one state in which they attract each other and form a molecule. That is, when two hydrogen atoms collide there is a 25 per cent probability that this collision will result in the formation of a molecule. Furthermore, in the molecule, the spin of the two electrons must be antiparallel. For this reason the normal state of the molecule is designated spectroscopically as a singlet state ($^1\Sigma_g$), whereas the repulsive state is of the triplet type ($^3\Sigma_u$)." [1]

(3) **Method of Molecular Orbitals:** As pointed out above, the simple Heitler-London theory leads to a value for the energy of formation of H_2 from its atoms, which is about 68 per cent of that observed experimentally. In seeking for an explanation of this discrepancy it is essential to note that, after all, the Heitler-London function may not be the best one by which to represent the charge density distribution which exists in the molecule. As discussed in Section 15(7) the most satisfactory form of ϕ^0 is that which results in a minimum value of E, that is, the highest value of the binding energy for the two atoms. Since

$$E = \bar{T} + \bar{V}, \qquad (19.8)$$

where $\bar{T}$ and $\bar{V}$ represent the average kinetic and average potential energy respectively, the function ϕ^0, or rather $|\phi^0|^2$, corresponds in all cases to such a compromise between the values of $\bar{T}$ and $\bar{V}$ as will yield a minimum value for E.

Now, from the fact that the Heitler-London treatment fails to give the correct value of E it must be concluded that the assumed form for ϕ^0 is not the most satisfactory one. And when the problem of the interaction of two hydrogen atoms is considered in further detail it becomes evident that there are certain aspects which have not been taken into account by Heitler and London.

For one thing, as pointed out by N. Rosen,[2] the two atoms, when sufficiently close, must exert a polarizing effect on each other. That is, the charge-density distribution for each of them is distorted by the field due to the other. By choosing a form of eigenfunction which would take this into account, Rosen was able to deduce an increase in the energy of binding to 4.02 volts.

Furthermore, in the Heitler-London treatment two other important effects have been neglected.[3] In the first place, no allowance has been made for the probability of the simultaneous occurrence of both electrons on the same nucleus. This would correspond to the two *equally possible* alternatives, A :B, that is, A^+B^-, and A: B, that is, A^-B^+. In other words, while the Heitler-London theory assumes a *purely homopolar* type of bond, it is conceivable that *polar* bonds are also present, or rather that the energy of binding

[1] Ref. S. D., p. 319.

[2] *Phys. Rev.*, **38**, 2099 (1931).

[3] Ref. W. G. P., p. 18.

is due to a combination of both types of bonds. The manner in which the wave functions should be modified to take this effect into account is discussed below.

In the second place, the Heitler-London method neglects consideration of the fact that the two electrons in H_2 possess antiparallel spins. Now two such unpaired electrons behave differently with regard to localization in the region between the nuclei from two electrons of similar spin. This effect has been described by J. C. Slater in the following remarks: [1]

"An electron," he writes, "can keep other electrons away from it in *two ways*: by the exclusion principle, and by the repulsive forces coming from electrostatics. The first acts only between electrons of the same spin, and approximately the same momentum, the second between any pair of electrons. The electrostatic effect is the one responsible for polarization, since this can take place before there is any real penetration of the charge distribution. The exclusion effect is primarily responsible for the formation of a hole around the penetrating electron. . . . The accurate calculations on the structure of the helium, almost the only case where the correlation between electrons of opposite spin has been very carefully studied, have shown that *the probability of finding an electron of one spin near one of opposite spin decreases, though not to zero, as the two come together.* The fact that there is a finite probability of finding them in contact, with an infinitely high potential energy, is compensated by the fact that they have an infinitely great negative kinetic energy at this point, a possible thing in wave mechanics, though not in classical mechanics."

Thus, if we have an electron at a distance r from a second electron, then for small values of r the probability that the latter has opposite spin is greater than the probability for one of similar spin. As a result, there must be included in the expression for total energy, a so-called *correlation energy* which takes into account the effect due to the Pauli exclusion principle.

Actually, it has proved difficult to use one-electron wave functions or atomic *orbitals* which satisfy all these requirements and F. Hund, S. R. Mulliken [2] and others have developed an alternative method which is known as that of *molecular orbitals.*

In this method the wave function expresses the motion of each electron in the field resulting from all the nuclei and the other electrons present in the molecule. The point of view is therefore analogous to that of Hartree in case of atomic systems. [3]

Instead of regarding the molecule H_2 as formed from two hydrogen atoms, we start with two protons at a given distance and consider the behavior of the system resulting from addition of one electron to form $H_2{}^+$ and of a second electron to form H_2. We therefore represent the eigenfunction for the molecule by

$$\Psi = \psi_1(x_1 y_1 z_1)\psi_2(x_2 y_2 z_2), \qquad (19.9)$$

[1] *Rev. Mod. Phys.*, **6**, 209 (1934). See especially pp. 227–8; italics are due to the writer.

[2] *Rev. Mod. Phys.*, **4**, 1 (1932). See also ref. V. V. S. and ref. W. G. P., Chap. III.

[3] Discussion taken from ref. S. D., p. 330 *et seq.*

where a capital Ψ is used, as Van Vleck and Sherman have suggested, to denote the molecular orbital, and small ψ corresponds to the wave function for each electron moving in the field due to the two nuclei and the other electron.

Let ϕ_A denote the atomic orbital for the motion of one electron in the field of nucleus A, and ϕ_B the atomic orbital with respect to nucleus B. Then equation (19.9) becomes

$$\Psi = [\alpha\phi_A(1) + \beta\phi_B(1)][\alpha\phi_A(2) + \beta\phi_B(2)]$$
$$= \alpha^2\phi_A(1)\phi_A(2) + \beta^2\phi_B(1)\phi_B(2)$$
$$+ \alpha\beta[\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)]. \quad (19.10)$$

In this equation α and β are arbitrary parameters, and it will be observed that $\phi_A(1)\phi_A(2)$ implies that both electrons are associated with nucleus A. Hence the first two terms on the right-hand side of equation (19.10) represent *ionic states*. On the other hand, the expression to the extreme right, in square brackets, represents a *homopolar* state, that is, the Heitler-London or shared-electron bond. Equation (19.10) may be expressed more concisely in the form

$$\Psi = a\psi_i + b\psi_{HL}, \quad (19.11)$$

where ψ_i designates the sum of the wave functions for the ionic state, and ψ_{HL} that for the homopolar state. Furthermore the relative probabilities for the occurrence of these two states are $a^2/(a^2 + b^2)$ for the ionic and $b^2/(a^2 + b^2)$ for the homopolar state.

The type of function represented by equation (19.11) is evidently more general since it signifies that the behavior of the system corresponds to a composite, as it were, of two different types of binding between the atoms. As $a^2/(a^2+b^2)$ varies from 1 to 0, we pass from a completely ionic to a completely homopolar type of molecule. Thus the old question as to whether HCl should be represented by H : Cl or H$^+$Cl$^-$ is answered, from the point of view of quantum mechanics, by the statement that the best representation probably involves both types of bond. As Van Vleck and Sherman remark, "One great service of quantum mechanics is to show very explicitly that *all gradations of polarity are possible*, so that in a certain sense it is meaningless to talk of such *idealizations* as homopolar bond, heteropolar bond, covalent bond, dative bond, etc." [1]

The introduction of ionic along with Heitler-London terms in the function Ψ represents an attempt to take care of electronic repulsion without having to introduce the so-called r_{12} term. This, however, leads in many cases to an overemphasis of ionic terms and a consequent lower energy of binding than that observed.

A comparison of the results obtained by the method of atomic orbitals and by that of molecular orbitals has been made by the same authors and their conclusion is as follows: [2]

---

[1] Ref. V. V. S., p. 171. The author is responsible for the italicized parts.

[2] Ref. V. V. S., p. 171.

"It is hard to say categorically whether the method of molecular orbitals or the Heitler-London method is the better. The latter undoubtedly is much preferable at very large distances of separation of the atoms, at least in symmetrical molecules, for then the continual transfer of electronic charge from one atom to another demanded by the ionic terms surely scarcely occurs at all. On the other hand, at small distances, the Heitler-London method probably represents excessive fear of the r_{12} effect, and the factorization into n one-electron problems presupposed by the method of molecular orbitals may sometimes be quite a good approximation. The molecular orbitals are often the more convenient for purposes of qualitative discussion, whereas the H-L method has been used the more frequently for purposes of quantitative calculation, partly, but by no means entirely, because of habit."

In any case an expression is sought for the function Ψ which, when substituted in the Schroedinger equation for the system, will minimize the value of E. As Penney points out,

"It is not necessary to use in the molecular wave function simply atomic wave functions of the ground states of the isolated atoms; instead, for any particular atom one can use a linear combination of all the possible wave functions with arbitrary coefficients. This implies that the atomic electrons are existing partly in excited states, and such *promotion*, as it is called, requires energy. However, the molecular bonds often gain considerable additional strength by suitable promotion, and when this is so, there is a net gain in stability to the molecule by allowing just the right amount of promotion to occur."

J. C. Slater [1] has derived expressions for the energy of a system consisting of two, three, or four univalent atoms in each of which the valence electron is in the *s*-state. The resulting expression for the binding energy involves both Coulomb and exchange integrals which are similar in nature to those occurring in the Heitler-London treatment of hydrogen. Such computations must however be regarded as only a first approximation to the true values, since they omit any consideration of correlation energy terms. That the inclusion in the calculation of these latter terms offers grave mathematical difficulties is, of course, the main reason for the failure on the part of "theoreticians" to attempt this task. However, it should be realized that all calculations of binding energies, and energies of activation which are based on this artificial device of dividing the energy into Coulomb and exchange energy are liable to be only the roughest kind of approximations to the true values.[2]

The present status of this whole problem has been very well described by Van Vleck and Sherman at the beginning of their comprehensive review. We cannot do better than quote their remarks.

"The subject of valence is really concerned with energy relations. If we knew the energies of all the possible different kinds of electron orbits in molecules, and also in the atoms out of which the molecule is formed, the rules of valence would automatically follow.

"Now the principles of quantum mechanics enable one to write down an equation for any system of nuclei and electrons, the solution of which would provide us with complete information concerning the stability of the system, spatial arrangements of the nuclei, etc. . . .

[1] *Phys. Rev.*, **38**, 1109 (1931).
[2] See the criticism of such calculations by A. S. Coolidge and H. M. James (*J. Chem. Phys.*, **2**, 811 (1934)).

"The complexities of the n-body problem are, alas, so great that only for the very simplest molecule, namely H_2, has it proved possible to integrate the Schroedinger wave equation with any real quantitative accuracy. Hence to date, anyone is doomed to disappointment who is looking in Diogenes-like fashion for honest, straightforward calculations of heats of dissociation from the basic postulates of quantum mechanics. How, then, can it be said that we have a quantum theory of valence? The answer is that to be satisfied one must adopt the mental attitude and procedure of an optimist rather than a pessimist. The latter demands a rigorous postulational theory, and calculations devoid of any questionable approximations or of empirical appeals to known facts. The optimist, on the other hand, is satisfied with approximate solutions of the wave equation. If they favor, say, tetrahedral and plane hexagonal models of methane and benzene, respectively, or a certain order of sequence among activation energies, or a paramagnetic oxygen molecule he is content that these same properties will be possessed by more accurate solutions. He appeals freely to experiment to determine constants, the direct calculation of which would be too difficult. The pessimist, on the other hand, is eternally worried because the omitted terms in the approximations are usually rather large, so that any pretense of rigor should be lacking. The optimist replies that the approximate calculations do nevertheless give one an excellent 'steer' and a very good idea of 'how things go,' permitting the systematization and understanding of what would otherwise be a maze of experimental data codified by purely empirical valence rules. In particular, he finds that a mechanism is really provided by quantum mechanics for the Lewis electron pair bond, and for the stereochemistry of complicated organic compounds. It is, of course, futile to argue whether the optimist or pessimist is right. . . . One thing is clear. In the absence of rigorous computations, it is obviously advantageous to use as many methods of approximation as possible. If they agree in predicting some property (for instance, the tetrahedral structure of methane) we can feel some confidence that the same property would be exhibited by a more rigorous solution,—otherwise none. . . ."

(4) **Transition in Type of Bond:** In the case of H_2, the contribution to the total energy made by the ionic terms is only about 4 per cent;[1] but in many other cases the values of a and b in equation (19.11) are comparable, and we may describe the bond *"as resonating between the covalent extreme and the ionic extreme."*[2] Under these conditions the actual bond energy is *greater than it would be for either type alone.* The increase is due to an interaction energy, or *resonance*, between the two structures, which stabilizes the molecule.

An interesting illustration of the transition from one bond type to the other is found, as Pauling has shown, in the case of the hydrogen halides.[3] It is possible to calculate, for each of these molecules, a "Morse" potential energy curve, similar to that shown in Fig. 19.4, for the ionic type of bonding, and another curve for the covalent type of bonding. For HF, these two energy curves lie close together, whereas in the case of HI, the curve for the ionic bonding lies considerably above that for the covalent bonding. Hence, it is concluded that the *ionic structure* H^+F^- *makes a larger* contribution to the normal state of the molecule than the covalent structure $H : F$.[4]

The transition from ionic to covalent type of bond in the series HF, HCl, HBr, HI is shown by the data on bond energies given in Table 19.1.[5]

[1] Ref. L. P., p. 42.
[2] *Ibid.*, p. 35.
[3] *J. Am. Chem. Soc.*, **54**, 988 (1932).
[4] Ref. L. P., p. 43.
[5] *Ibid.*, p. 49.

TABLE 19.1

	H — H	F — F	Cl — Cl	Br — Br	I — I
Bond energy:	103.4	63.5	57.8	46.1	36.2
		H — F	H — Cl	H — Br	H — I
Bond energy (obs.):		147.5	102.7	87.3	71.4
(calc.):		83.5	80.6	74.8	69.8
Δ:		64.0	22.1	12.5	1.6

The first line gives the bond energies for the diatomic molecules of type A — A. For a molecule of type A — B, in which the two atoms are unlike, we would expect the energy for a *normal covalent bond* to be equal to the average of the energies for the bonds A : A and B : B. For the case of H — F, the calculated energy would therefore be $\frac{1}{2}(103.4 + 63.5) = 83.5$. The difference, Δ, between this value and the observed value is 64.0, as shown in the table. This additional energy must be due, according to Pauling, to the ionic character of the bond. In other words, Δ is a measure of "the *additional ionic resonance energy* which the bond has as compared with a bond between like atoms." The data in the table thus show that the bond loses its ionic character as we pass from HF to HCl and HBr, and becomes practically normal covalent for HI.

For the alkali halide molecules in the vapor state Pauling concludes from similar considerations that "the bonds in all of these molecules are essentially ionic, with only a small amount of covalent character."

(5) **The Directed Covalent Bond:** As shown by Heitler and London, the energy of a covalent bond is largely that due to the exchange or resonance of two unpaired electrons between the two atoms. The magnitude of this energy increases with the amount of *overlapping* of the two atomic orbitals or eigenfunctions associated with the two electrons. · That is, the energy increases with the concentration of charge distribution in the region between the two nuclei. Consequently it is to be expected, according to Pauling,[1] "that of *two orbitals in an atom the one which can overlap more with an orbital of another atom will form the stronger bond with that atom, and, moreover, the bond formed by a given orbital will tend to lie in that direction in which the orbital is concentrated.*"

In this section we shall consider the theory of directed covalent bonds which Pauling has developed, on the basis of this postulate, in a series of papers published since 1931.[2] In the first of these papers six postulates were introduced to be used as a guide in the determination of relative energies and directions of bonds in the formation of molecules.

---

[1] Ref. L. P., Chap. III. The discussion in this section is based largely upon the remarks in this chapter.

[2] *J. Am. Chem. Soc.*, **53**, 1367 (1931).

The first three of these postulates have already been incorporated in the discussion of the Heitler-London theory of the covalent bond. The second three involve essentially a more precise statement of the manner in which bond directions may be deduced from atomic orbitals. These rules, "which are justified by the qualitative considerations of the factors influencing bond energies," are as follows:

1. The main resonance terms for a single electron-pair bond are those involving only one eigenfunction from each atom.

2. Of two eigenfunctions with the same dependence on r, the one with the larger value in the bond direction will give rise to a stronger bond, and for a given eigenfunction the bond will tend to be formed in the direction with the largest value of the eigenfunction.

3. Of two eigenfunctions with the same dependence on θ and η,[1] the one with the smaller mean value of r, that is, the one corresponding to the lower energy level for the atom, will give rise to the stronger bond.

Now let us consider the application of these rules to the determination of bond directions in such molecules as H_2O and NH_3. In the case of the oxygen atom, the electron configuration is $2s^2 2p^4$. The $2s$ electrons are paired, and except under certain special conditions which are discussed below, they do not take part in bond formation. While the s-orbital is spherically symmetrical, and therefore possesses no preferred direction for bond formation, the three p orbitals (p_x, p_y and p_z) are directed, as shown in Figs. 10.2 and 10.3, along the three Cartesian axes. They will therefore tend to form bonds in these directions, and it follows from the form of the expression for the p-eigenfunction that the strength of an s-p bond will be about $\sqrt{3}$ times that of an s-s bond.

We would thus expect a structure for H_2O of the form $: \overset{..}{O} : H$ in which the
$\overset{}{H}$
two OH axes form an angle of 90°. The observed angle is 105°.

According to Pauling, "the difference of 15° between the observed value of the bond angle and the expected value of 90° is probably to be attributed in the main to the partial ionic character of the $O-H$ bonds, estimated to be 39 per cent. This would give a resultant positive charge to the hydrogen atoms, which would repel one another and thus cause an increase in bond angle."[2]

On the other hand, in H_2S, the angle between the two SH axes is observed to have the value 92° 20', which indicates that in this case the bonds are nearly normal covalent. For the same reason it would be expected that the three s-p bonds in NH_3 (corresponding to the three $2p$ electrons in the valence shell of nitrogen) should be oriented at right angles to each other. This would yield a pyramidal structure for the molecule, each axis making an angle of 54.7° with the axis of the pyramid. The experimental value is 67°, which

---

[1] See Section 10(1) for interpretation of these angle variables.
[2] Ref. L. P., p. 78.

corresponds to 108° between the bond axes.   The discrepancy is attributed to the same cause as in H_2O.

The electron configuration for carbon in the normal state is $2s^2 2p^2$, which indicates the presence of two unpaired electrons in the $2p$ state.   This accounts for the doubled bond in C : : O.   In the case of CH_4, the evidence from organic chemistry leads to the conclusion that the four bonds are equivalent and directed towards the corners of a regular tetrahedron.   To account for this Pauling introduces a new concept—that of "hybridization" of eigenfunctions to form new atomic orbitals which take the place of the original s and p orbitals.

As mentioned above an s-p bond has a strength of about $\sqrt{3}$ times that of an s-s bond.   This corresponds to a ratio of 3 to 1 in the energies of the bonds. "It is found," as Pauling states, "that a bond orbital formed by linear combination of s and p orbitals, taken with a certain ratio of numerical coefficients, has a bond strength greater than that for an s or p orbital alone, the strength of the best s-p hybrid bond orbital being as great as 2." [1]

It is assumed that the wave function for each bond can be represented by one of the four combinations,

$$\Psi_i = a_i s + b_i p_x + c_i p_y + d_i p_z, \tag{19.12}$$

where $i = 1$, 2, 3 or 4, and the numerical coefficients are subject to the requirements,

$$\int \Psi_i^2 d\tau = 1, \text{ or } a_i^2 + b_i^2 + c_i^2 + d_i^2 = 1 \tag{19.13}$$

and

$$\int \Psi_i \Psi_k d\tau = 0, \text{ or } a_i a_k + b_i b_k + c_i c_k + d_i d_k = 0, \tag{19.14}$$

where $i \neq k$, and $i, k = 1, 2, 3, 4$.

These relations state that (1) the total charge density associated with the bond shall be equal to unity, and (2) that the wave functions for any two bonds shall not overlap.[2]

For the first bond the direction may be chosen arbitrarily and if we take it along the x-axis, it is found that the orbital

$$\Psi_1 = \frac{1}{2} s + \frac{\sqrt{3}}{2} p_x \tag{19.15}$$

has a maximum value,

$$M_1 = \frac{1}{2} + \frac{\sqrt{3}\sqrt{3}}{2} = 2,$$

which is considerably greater than the value $\sqrt{3}$ for a pure p orbital, or 1 for a

[1] Ref. L. P., p. 82.
[2] The following remarks are based on the discussion by S. D., *op. cit.*, pp. 361–364.

pure s orbital. Fig. 19.7 shows a plot of this function in the xz-plane. It will be observed that the orbital is concentrated in the bond direction (which is an axis of rotational symmetrically) and it follows that such an orbital will overlap considerably with, for instance, the s orbital of a hydrogen atom.

This hybridization is made possible by the fact that only about 1.6 volts (36,900 cal./mole is required to excite one of the $2s$ electrons to a $2p$ state. This energy is considerably less than the energy of the $C-H$ bond (87,300 cal./mole) and Pauling assumes that when the energy required for "promotion" of an electron is less than the interaction energy due to bond formation such hybridization will occur.

$$\psi = \tfrac{1}{2} s + \tfrac{\sqrt{3}}{2} p_x$$

Fig. 19.7. Tetrahedral sp Eigenfunction

A second bond function may be introduced *in the same plane*, of the form

$$\Psi_2 = a_2 s + b_2 p_x + d_2 p_z. \tag{19.16}$$

Now, it is found that for maximum energy this function has the same form as the first one but is concentrated along an axis which makes an angle of 109°28′ with that of the first bond, *which is just the anlge between the lines drawn from the center to two corners of a regular tetrahedron.* The actual expression for the bond function has the form,

$$\Psi_2 = \frac{1}{2} s - \frac{1}{2\sqrt{3}} p_x + \frac{\sqrt{2}}{\sqrt{3}} p_z . \tag{19.17}$$

The two orbitals, which are directed toward the other two corners of the tetrahedron, are given by the relations,

$$\Psi_3 = \frac{1}{2} s - \frac{1}{2\sqrt{3}} p_x + \frac{1}{\sqrt{2}} p_y - \frac{1}{\sqrt{6}} p_z \tag{19.18}$$

and

$$\Psi_4 = \frac{1}{2} s - \frac{1}{2\sqrt{3}} p_x - \frac{1}{\sqrt{2}} p_y - \frac{1}{\sqrt{6}} p_z. \tag{19.19}$$

All four orbitals are identical except for orientation. "This calculation," as Pauling remarks, "provides the quantum mechanical justification of the chemist's tetrahedral carbon atom, present in diamond and all aliphatic carbon compounds, "as well as for a number of other tetrahedral atoms and ions. Furthermore, since "each of these tetrahedral bond eigenfunctions is cylindrically symmetrical about its bond direction, the bond energy is independent of orientation about this direction, so that there will be *free rotation about a bond.*" On the other hand, there can be no free rotation about a double bond.

In a similar manner it is possible to have hybrid bonds involving d orbitals. As mentioned previously, the d group in an atomic system is completely filled by ten electrons. With these there are associated *five d* orbitals, as shown in Fig. 10.3. The maximum bond strength of a d orbital is 2.236. That of the strongest d-s-p hybrid orbital is 3, as shown by Pauling. Hence, when as in the case of the transition elements (e.g., Fe, Co, Ni) $3d$ orbitals are available which have energies not very different from the $3p$ and $4s$ orbitals, it is possible to obtain from these, by hybridization, much stronger covalent bonds than with s and p orbitals only.

"It is found," as Pauling states,[1] "on analysis of the mathematical problem that when only two d orbitals are available for combination with s and p, six equivalent bond orbitals of strength 2.923 (nearly as great as the maximum 3) can be formed, and that *these six orbitals have their bond directions toward the corners of a regular octahedron.* From this theoretical discussion we accordingly conclude that complexes such as $[Co(NH_3)_6]^{+++}$, $[PdCl_6]^{--}$, $[PtCl_6]^{--}$, etc., should be octahedral in configuration. This conclusion is of course identical with the postulate made by Werner to account for isomerism in complexes with different substituent groups, and verified also by the X-ray examination of $Co(NH_3)_6I_3$, $(NH_4)_2PdCl_6$, $(NH_4)_2PtCl_6$, and other crystals."

In his book, which has been referred to frequently in the above remarks, Pauling has given many other illustrations of the application of this theory of directed valence bonds, which has thus provided a theoretical basis for conclusions which chemists had already deduced by intuitive methods. However, Pauling's theory leads to quantitative relations between bond energies, and it is of interest to note that to a large extent these conclusions are in agreement with actual measurements of bond energies.

The structures of molecules such as H_2O and CH_4 have also been investigated by J. H. Van Vleck,[2] as well as by W. Heitler, E. Hückel and G. Rumer. The mathematical technique used by these investigators is quite complex, but the conclusions deduced are not essentially different from those deduced by Pauling.

(6) **Resonance Energy:** In sub-section (3) it was pointed out that resonance between ionic and covalent types of binding increases the stability of a molecule. Resonance may also occur when it is possible to assign to a molecule two or more structures which differ in distribution of valence bonds. One of the most important illustrations of this form of resonance is provided by the benzene molecule. As is well known, five apparently different structures have been suggested for this molecule, of which the one most generally accepted is that of Kekulé.

On the basis of quantum mechanics the solution of the problem confronting chemists in this case as well as in those of a number of other molecules has been obtained by the following solution: "*the actual normal state of the molecule is not represented by any one of the alternative reasonable structures, but can be repre-*

[1] Ref. L. P., p. 92.
[2] Ref. V. V. S., pp. 196–7.

sented by a combination of them, their individual contributions being determined by their nature and stability. The molecule is then described *as resonating among the several valence-bond structures.*" [1]

Thus in the case of benzene Pauling assumes that in the normal state the eigenfunction for the molecule may be represented by a combination of five simple functions in the form

$$\Psi = a(\psi_A + \psi_B) + b(\psi_C + \psi_D + \psi_E), \tag{19.20}$$

where the functions ψ_A, ψ_B, etc., refer to the five "canonical" structures shown in Fig. 19.8. It will be observed that the structures A and B are of the Kekulé type, and C, D, E are of the Dewar type.
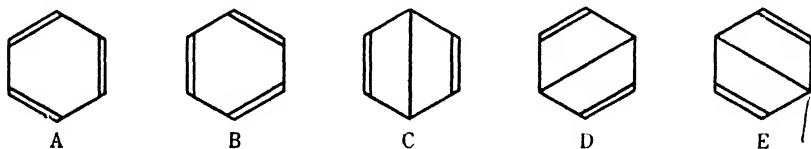
FIG. 19.8. Five Canonical Valence-Bond Structures for Benzene, Leading to Resonance Phenomenon

Equation (19.20) indicates (1) that the molecule behaves as if it were a composite of the five canonical structures, (2) that structures A and B are equally probable; (3) that C, D, E, are also equally probable, and (4) that the relative probabilities of the Kekulé and Dewar structures are in the ratio $2a^2 : 3b^2$.

According to L. Pauling and G. Wheland,[2] the values of the coefficients in equation (19.20) are $a = 1$, $b = 0.4341$, which indicates that on the average the benzene molecule occurs much more frequently in the structure assigned by Kekulé than in any other form.

The increased energy of binding of the atoms due to this resonance effect has been determined empirically from the following data:

The energies (determined from measurements on aliphatic hydrocarbons) of the different bonds, in kcal. per mole, are as follows: $C-H$, 87.3; $C-C$, 58.6; and $C=C$, 100. Hence the total energy of formation of a Kekulé structure should be given by $(6 \times 87.3) + (3 \times 58.6) + (3 \times 100) = 1000$ kcal. per mole. The actually observed heat of formation from the heat of combustion and heats of formation of the products of combustion is 1039 kcal. per mole. Hence the resonance energy is about 39 kcal. per mole. According to measurements of heat of hydrogenation, by G. B. Kistiakowsky and his collaborators,[3]

[1] Ref. L. P., p. 117. The idea of quantum-mechanical resonance was developed around 1931 by L. Pauling, J. C. Slater, and E. Hückel. A comprehensive list of references on this point is given by Pauling in a footnote on the page cited.

[2] *J. Chem. Phys.*, **1**, 362 (1933).

[3] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *J. Am. Chem. Soc.*, **57**, 856 (1935); **58**, 137, 146 (1936).

the resonance energy is 35.97 kcal. per mole.   Designating the *exchange energy* for two *adjacent* hydrogen atoms in the ring by α, Pauling and Wheland [1] have deduced for the resonance energy of the molecule the value $1.1055\ \alpha = 38.2$ kcal. per mole.   The substantial agreement between these values must be regarded as confirmation of the general validity of the concept of the quantum-mechanical resonance.

In a similar manner, Pauling and his associates have derived values of the resonance energy for molecules consisting of two or more benzene rings and for a considerable number of other molecules in which double bonds alternate with single bonds.

Observations of another nature which are in agreement with the concept of resonance are those made on interatomic distance in benzene.[2]   For a single bond, $C-C$, the interatomic distance is 1.54 Å; for a double bond, $C\!\!=\!\!C$, this distance is 1.34 Å.   The observed value for benzene is 1.39 Å, which is in accord with the assumption that the structure is of the Kekulé type to a considerable extent and that, furthermore, the double-bond potential function is more effective than that arising from the single bond.

[1] *Loc. cit.*
[2] Ref. L. P., pp. 161–4.

CHAPTER III

THE FIRST AND SECOND LAWS OF THERMODYNAMICS

BY HUGH S. TAYLOR

David B. Jones Professor of Chemistry, Princeton University, N. J.

It is not possible completely to define any system by sole reference to the material content of the system, its atomic or molecular constituents. Associated with matter, independent of the fixed and unchangeable attributes of mass and form characteristic of the particular species, are other properties which change with circumstances. Thus, for example, the temperature, pressure, heat content, motion, electrical potential, color, may vary, without variation in the actual atomic or molecular content of the system. The properties of a copper rod when hot differ from those of a cold rod, those of a metal at high electrical potential from those of a metal uncharged. Motion and position convey definite properties to matter as can be illustrated by means of a rifle bullet or an avalanche. Even at a constant temperature the form of matter may vary. Gaseous, liquid and solid mercury either separate or coexistent are possible at a given temperature. The compression to which a given system is subjected may determine the changes which such a system will undergo. These variables, to which all forms of matter are subject and from which they cannot be entirely dissociated, are all energy variables of material things.

Every variation in the properties of a given species of matter is to be attributed to a variation of one or more of several energy variables. These energy variables are convertible one into the other, matter being the medium whereby such conversion is effected. Thus, heat energy is convertible into the energy of motion, the increased motion of the particles receiving such heat energy. Conversely, motion may be converted into heat energy by friction as was emphasized by Count Rumford in his inquiries concerning the heat resulting from the boring of cannon, or as demonstrated by Davy in the production of water by the friction of ice. Electrical energy can be expended in the production of heat energy or in the production of chemical change whereby energy may be stored. The energy of chemical change is the source of most of our heat energy and is an instrument in the production of electrical energy. Many chemical actions are productive of light or may be made to produce it by way of other energy forms. Before, however, this concept of interconvertibility of energy can be examined in its quantitative aspects, the method of definition of energy must be examined in some detail.

(1) **The Definition of Energy:** Every change in the condition of matter is to be ascribed to the operation of one or other forms of energy. The energy is

composite of two factors, an intensity factor and a capacity factor, and is, indeed, the product of these two factors. The intensity factor is the measure of the resistance offered to the change of condition resulting from the operation of the energy. The energy can only operate when this resistance is either withdrawn or overcome. Such an intensity factor tending to produce a change is known as a force. A force, overcoming a resistance to an extent which we may designate as the capacity factor, performs work, expends energy. With a given force, the energy expended or the work performed varies directly as the capacity factor. In the production of motion the energy expended depends, therefore, on the force required to produce motion against the resistance and on the distance through which the object acted upon is moved. In the raising of an object of mass m against gravity, g, through a height h, the force exerted in opposition to gravity is mg and the capacity factor is the height h.) The energy expended becomes, therefore, the product mgh. In the production of a volume change dv in any body against an external pressure p, the intensity factor or force, p, acts through a volume dv which is the capacity factor; the work done or energy expended is the product of the two factors, pdv. All energy changes of whatever form may be similarly resolved into two such factors.

The unit of energy in the c.g.s. system of units is the *erg*. It is the energy associated with a force of one *dyne* acting through one centimeter. A dyne is the force which, acting for one second on one gram, produces a velocity of one cm. per second in the body upon which the force is impressed. It is related to the action of gravity upon a mass. Gravity produces an acceleration of 980.6 cm. per sec. when acting upon a mass at sea-level and 45° latitude. The weight of one gram divided by $g = 980.6$ cm. per sec. is equivalent to one dyne. If the pressure of the atmosphere be defined as the pressure of 760 mm. of mercury under standard conditions, it may be expressed in dynes per sq. cm.

$$1 \text{ atm.} = 76 \times 13.59 = 1033.3 \text{ grams per sq. cm.}$$
$$= 980.6 \times 1033.3 = 1013300 \text{ dynes per sq. cm.}$$

Since the unit of energy is the product of a force and a distance it has the dimensions of a force (mass $\times$ acceleration $= m \times lt^{-2}$) multiplied by a length, l, and therefore the dimensions ml^2t^{-2}, mass $\times$ (length)^2/(time)^2. All forms of energy have these same dimensions no matter what the type of energy involved. As will subsequently appear, other energy units are employed for various types of energy. Their correlation involves the generalization, resulting from human experience, which is known as the First Law of Thermodynamics.

THE FIRST LAW OF THERMODYNAMICS

(2) **The Mechanical Equivalent of Heat:** The first statement of the equivalence of heat and mechanical work is to be attributed to Mayer, 1842, who also attempted to ascertain the proportionality factor connecting the two energy quantities. Carnot (died 1832), in a posthumous publication, enunciated the same principle: "Heat is simply motive power or motion which has changed

its form, for it is but a movement amongst the particles of a body. Whenever motive power is destroyed, an equivalent quantity of heat is produced; and, reciprocally, whenever heat is destroyed, motive power is developed." Mayer calculated the work involved in the expansion process when the specific heat of a gas is measured at constant pressure, this work, w, being then equated to the difference of the specific heats at constant pressure and constant volume, $c_p - c_v$, multiplied by the proportionality factor J, the mechanical equivalent of heat,

$$w = J(c_p - c_v). \tag{2.1}$$

The assumption involved in this calculation, namely, that heat energy and mechanical energy are equivalent, received its first experimental test by Joule, 1843–1880. He measured the heat produced q by most divergent mechanical processes and showed that in each case the proportionality factor, J, was approximately constant,

$$w = Jq. \tag{2.2}$$

Joule's experiments included the following:

(1) The heat produced when various liquids, water, oil and mercury, were stirred was compared with the work involved in producing the stirring by falling weights.

(2) The heat produced in a coil of wire by induction currents set up by rotation of the wire between the poles of an electromagnet was compared with the work done by falling weights in rotating the coil. The heat produced was measured by the rise in temperature of water in which the coil was rotated.

(3) The heat produced by compression of water through narrow openings or capillaries was compared with the work required to drive the water through the openings or capillaries.

(4) The heat produced by compressing air to 22 atmospheres was compared with the work of compression.

(5) The heat produced by the passage of an electric current through a coil of wire immersed in a calorimetric fluid was compared with the energy of the current consumed.

Joule concluded that "772 lbs. falling one foot would heat a pound of water one degree." Transformed into modern units Joule's measurements gave approximately

$$J = 4.17 \times 10^7 \text{ ergs per } 15° \text{ cal.} \tag{2.3}$$

The fact that independent methods of producing heat gave closely concordant values for J constituted the desired proof of the law of equivalence of heat energy and mechanical energy.

These early measurements have been repeated at intervals with greater refinements of technique. Rowland (1879), Miculescu (1892) and Reynolds and Moorby (1898) determined J by the water-stirring method. Greater accuracy is achieved with the electric heating method, which was employed by Griffiths (1893), Schuster and Gannon (1895), Callendar and Barnes (1902), and Dieterici (1905).

The necessity for defining the unit of energy in terms of the heat capacity of water (the 15° calorie being defined as the heat required to raise 1 g. of water from 14.5° to 15.5° C.) became less compelling some thirty years ago

when it became possible to measure quantities of energy more accurately by electrical methods. These energy measurements are based on the second as the unit of time and upon working standards of electromotive force and resistance maintained at various national standards laboratories and correlated by international agreements. The working standards are manganin wire resistance coils and saturated cadmium sulfate (Weston) cells which are calibrated in terms of the international ohm and the international volt.

The electrical method of energy measurement involves the definition of the intensity factor, electrical potential, and also the capacity factor, the quantity of current flowing under the given potential. The potential E and current C are related to the resistance R by means of Ohm's Law, discovered by Ohm in 1827. The law may be expressed by the relation,

$$C = E/R. \tag{2.4}$$

The unit of resistance, the ohm, is defined as the resistance at 0° C. of a column of mercury one square mm. in cross section, 106.3 cm. in length and weighing 14.4521 grams. The unit of electricity is the coulomb, the quantity of electricity which will deposit 1.11800 mg. of silver from a solution of silver nitrate in a standard coulometer. The number of coulombs required to deposit one g. equivalent of silver (107.88 g.) is obviously $107.88/0.001118 = 96494$ coulombs, and this quantity of electricity is known as the faraday. The unit of current is the ampere and is a current of one coulomb per second. The unit of potential, the volt, may then be defined, in reference to the units of current and resistance, as the potential which, applied to a conductor of unit resistance, will cause a current of one ampere to flow. It is defined practically in terms of the electromotive force of a cell which yields electrical energy equivalent to 1 joule (10^7 ergs) when the quantity of electricity produced is one coulomb. Herein lies the relation of electrical to mechanical energy. 1 volt-coulomb = 1 volt-ampere-second = 1 absolute joule = 10^7 ergs.

The Weston cell is the standard cell chosen for its reproducibility to serve as the standard of electromotive force. The cell consists of: 12 per cent Cadmium amalgam | $CdSO_4 \cdot \frac{8}{3}H_2O$ + Saturated Solution | Hg_2SO_4 | Hg and by international agreement, in 1908, was stated to have an electromotive force of 1.0183 volts at 20° C. In terms of this definition of voltage it is now known, by reason of subsequent more accurate measurements of the standards involved, that the associated international joule is actually greater than the absolute joule defined above. The U. S. Bureau of Standards, in 1930, while continuing to report all thermochemical data in terms of the international joule, concluded that, on the basis of available measurements, 1 international joule = 1.0004 absolute joules = 1.0004×10^7 ergs. At the same time it was decided to define the calorie arbitrarily by the relation

$$4.1850 \text{ absolute joules} \equiv 1 \text{ calorie}. \tag{2.5}$$

In terms of international joules, therefore, the relation is 4.1833 international joules = 4.1850 absolute joules ≡ 1 calorie.

The absolute unit of quantity of electricity, the so-called electrostatic unit, is that quantity which exerts a force of one dyne upon a quantity of equal magnitude at a distance of one centimeter. This follows immediately from the equation for the electrostatic force F between two charges e_1 and e_2 at a distance r, namely $F = e_1 e_2 / K r^2$ where K is set equal to unity in a vacuum. Since the dimensions of force are mlt^{-2}, it follows that the quantity e must have the dimensions $(ml^3 t^{-2})^{1/2}$ or $m^{1/2} l^{3/2} t^{-1}$. It follows also that the dimensions of current or quantity per sec. must be $m^{1/2} l^{3/2} t^{-2}$.

Similarly, the electromagnetic force between two poles of strength m_1 and m_2 is given by $F = m_1 m_2 / \mu r^2$, where μ is set equal to unity in a vacuum. Again the dimensions of the pole strength will be $m^{1/2} l^{3/2} t^{-1}$. The product of pole strength and current has the dimensions of work, i.e., $ml^2 t^{-2}$. Hence the dimensions of current in this case are $ml^2 t^{-2} / m^{1/2} l^{3/2} t^{-1} = m^{1/2} l^{1/2} t^{-1}$. It will be noted therefore that the electromagnetic unit is related dimensionally to the electrostatic unit as $m^{1/2} l^{1/2} t^{-1} : m^{1/2} l^{3/2} t^{-2}$ or as $1 : lt^{-1}$, which latter term has the dimensions of a velocity, actually, the velocity of light $c = 2.998 \times 10^{10}$ cm. sec.$^{-1}$. Hence 1 e.s.u. : 1 e.m.u. $= 1 : c$. The practical unit of current, the ampere, is defined as one-tenth of the electromagnetic unit of current.

Since current and potential are reciprocally related by means of Ohm's Law it follows that the electromagnetic unit of potential must be $1/(3 \times 10^{10}) = 0.33 \times 10^{-10}$ electrostatic unit of potential. The practical unit of potential, the volt, is defined as 10^8 electromagnetic units of potential and therefore 300 electrostatic units of potential.

Since a pressure of 1 atmosphere $= 1013300$ dynes per sq. cm.,

$$1 \text{ cc.-atm.} = 1013300 \text{ ergs} = 0.10133 \text{ joules.}$$

For a perfect gas, the fundamental equation connecting pressure, volume and temperature is, for one mole

$$pv = RT,$$

where R is the gas constant. On the absolute temperature scale, $0°$ C. $= 273.16°$. For one mole of gas under standard conditions the accepted value of $v = 22414$ cc. Hence,

$$R = \frac{22414 \times 1}{273.16} = 82.06 \text{ cc. atmos. per degree.}$$

When transformed into the units of heat energy with the data already supplied

$$R = 1.9869 \text{ calories per degree}$$

or

$$R = 8.3145 \text{ abs. joules per degree}$$
$$= 8.3128 \text{ int. joules per degree.}$$

(3) **The Law of Conservation of Energy:** This law, the first law of thermodynamics, of which the equivalence of heat and mechanical energy is a special

case, was definitely enunciated by Helmholtz in a publication "Über die Erhaltung der Kraft," [1] 1847. In this contribution, Helmholtz demonstrated that the law of equivalence of heat and mechanical energy was a direct consequence of the century-old experience of investigators that it is impossible to produce a perpetual motion machine which, without expenditure of energy, shall produce energy. Definite proof of the impossibility of constructing such a machine cannot be achieved. It is necessary to rely upon the cumulative experience of investigators that the search for such a machine is fruitless. Furthermore, by assuming the impossibility of perpetual motion of this type, conclusions may be drawn which may be verified and, in their turn, be employed for the discovery of further facts or laws. Thus is attained the definite and general belief as to the truth of the fundamental law.

Helmholtz pointed out that, if the mechanical equivalent of heat were not an invariable quantity, it would be possible by suitable coupling of two processes of energy transformation, heat into mechanical work, to arrange that the heat produced in the stage of energy consumption should be more than sufficient to produce, in the second stage of the process, the same amount of energy as was consumed in the first stage. A perpetual motion machine would result. Heat energy would be continuously produced without the expenditure of any other energy form. The impossibility of such a perpetual motion machine compels our belief in the exact equivalence of heat and mechanical energy. Helmholtz concluded therefore that: "In all processes occurring in an isolated system, the energy of the system remains constant."

The energy of a system is a function only of the state of the system at the given moment irrespective entirely of its past history, the manner or method of its origin. It is especially to be emphasized that this independence of past history refers only to systems whose identity is complete in all except the element of time. It is not enough that the atomic or molecular make-up shall be the same, for this may be secured even though the energies of the systems differ widely. Thus, for example, stick lead and electrolytic lead might be identical as to atomic content, pressure, temperature, and the like, but be different in energy content by reason of state of division, size of crystal and the like. Only with a complete identity in all factors except time can it follow that the energy is a function of the momentary state. The energy change is then a function of the initial and final states of the system. For, if it were possible to effect a change in any system from state A to state B such that the energy change involved was dependent on the path by which the change was achieved, it would again be possible to construct a perpetual motion machine. All that would be necessary would be that one such method of conducting the change could be reversed. Then, by a suitable coupling of two processes,

$$A \rightarrow B \text{ by path I,}$$
$$B \rightarrow A \text{ by path II,}$$

[1] *Ostwald's Klassiker*, No. 1.

if the energy produced in path I were larger than that consumed in path II, the system would be, on completion of the reverse process, in its initial state and a surplus of energy would be available. By repetition of the process, energy could be continuously produced—a perpetual motion would be possible This is denied by human experience as embodied in the first law of thermodynamics.

(4) **The Internal Energy of a System:** The change from state A to state B of a given system is therefore accompanied by a perfectly definite energy increment which we may designate by ΔE and define by the expression

$$\Delta E = E_B - E_A. \tag{4.1}$$

In such case, E_B and E_A represent the energies of the system in states B and A respectively. They may be more definitely designated as the internal energies of the system in the two states. They are energy quantities of unknown absolute magnitude. They include the energy resultant from such factors as motion of the molecules, position of the molecules, molecular attraction, intra-molecular, intra-atomic, and other unspecified forces. While, however, the absolute magnitude of such internal energy is not ascertainable, the change in such is definite and unchangeable for any given process of change.

Any such change in the internal energy of a system can only be achieved with a simultaneous change in the energy of surrounding systems, since the law of conservation of energy *must* be obeyed. An increment in internal energy of the system is secured, therefore, at the expense of a decrement in the energy of its surroundings. A decrement in the internal energy results in an increase of the energy of its surroundings. If we consider any process of change from state A to state B, whereby an increment of internal energy $\Delta E = E_B - E_A$ occurs, which results in the abstraction of heat, q, from the surroundings and simultaneously the performance of external work w by the system on the surroundings; then, by application of the law of conservation of energy,

$$\Delta E = q - w. \tag{4.2}$$

It has been shown that ΔE is a perfectly definite quantity for any given process of change, dependent only on the initial and final states, independent of the path. This is not true of either q or w. According as the experimental conditions change q and w will both vary. This may be illustrated, for example, by a change of state involving both temperature and pressure. Thus, to transform one gram of ice at 0° C. and 1 atm. pressure to water vapor at 25° C. and 15 mm. pressure there are several possible paths each of which will involve values of q and w characteristic of the path, all of which involve a definite and unchangeable value of ΔE. One path involves fusion at 0° C. and 1 atm. requiring the absorption of the latent heat of fusion, then the raising of the temperature of the water from 0° to 25° C. at 1 atm. pressure, involving the heat capacity of the water, and finally the evaporation of the water at 25° C. by change in the pressure. This stage involves latent heat of vaporization and all three steps involve smaller or larger changes in the work terms, w. An

alternative path involves a change in the pressure at 0° C. from 1·atm. to below the saturated vapor of ice with consequent vaporization. Subsequent steps involve raising the temperature of the water vapor to 25° C. and adjustment to the final pressure (15 mm.). This path has its own characteristic values of q and w, which will be different from those involved in the path first discussed. Quite generally, any particular path will have its own characteristic values of q and w, different from the values of these quantities for any other paths. Their algebraic sum, by the law of conservation of energy will be equal to the change in internal energy by equation (4.2).

If a process be carried out at constant volume and no energy factors other than those of mechanical energy are involved in the external work performed then, since $w = 0$, it follows that $\Delta E = q$; the whole increment of internal energy is secured at the expense of the heat of the surroundings.

If a process be conducted, not at constant volume, but at constant pressure, it will ordinarily be accompanied by a volume change. The external work done by the system on the surroundings will be $p(v_B - v_A) = p\Delta v$, p being the prevailing pressure and Δv the increase in the volume of the system during the change from state A to state B. The heat q abstracted from the surroundings will then be given by the expression

$$q = \Delta E + w = \Delta E + p\Delta v. \tag{4.3}$$

If a process be conducted so that heat is neither gained nor lost by the system to the surroundings the process is known as an *adiabatic* process. The quantity q is then zero. The work performed by the system on the surroundings is then done at the expense of the internal energy of the system, or

$$\Delta E = -w. \tag{4.4}$$

In the preceding paragraphs the quantity w has been limited to the case of changes in mechanical energy. It will later be shown that the quantity w may be composite of several forms of energy, of which electrical energy may be an important unit. The magnitude of the quantity w will be dependent on the mode of conduct of the process, on the extent to which the process is harnessed to produce the various forms of external work.

It is thus evident that while E, the internal energy of the system, is a single-valued function of its several variables, pressure, temperature, volume and the like, dependent only on its state at the moment, this is not true concerning the quantities q and w. Whereas the small change of internal energy, dE, has the properties of a complete differential,

$$dE = \frac{\partial E}{\partial x} dx + \frac{\partial E}{\partial y} dy + \frac{\partial E}{\partial z} dz + \cdots, \tag{4.5}$$

where x, y, z, etc., are the several variables, the same is not true of the heat absorbed or external work performed by the system when such change in internal energy occurs. These may vary widely, provided always that the

law of energy conservation, equation (4.2), is satisfied. The quantities q and w are dependent *entirely* on the path by which the process is achieved. For this reason infinitesimal quantities q and w are designated in the following by dq and dw.

(5) **The Heat Content of a System:** Returning now to consideration of a process involving an increase in internal energy, heat absorption from the surroundings and a volume change v_A to v_B against a constant external pressure p. The first law of thermodynamics demands that

$$\Delta E = E_B - E_A = q - p(v_B - v_A). \qquad (5.1)$$

This may be transformed thus:

$$(E_B + pv_B) - (E_A + pv_A) = q. \qquad (5.2)$$

In this case the heat, q, absorbed by the system, is evidently defined by the initial and final states of the system. If we define a quantity

$$H = E + pv \qquad (5.3)$$

and term this quantity, H, the heat content of the system, the equation becomes

$$H_B - H_A = q = \Delta H. \qquad (5.4)$$

It will be noted that the quantity ΔH, like ΔE, is dependent only on the initial and final states of the system. The heat content of the system, H, like E, is a single-valued function of its several variables.

(6) **The Heat Capacity of a System:** We may define the mean heat capacity, $\bar{c}$, of a system between two temperatures as the quantity of heat necessary to raise the system from the lower to the higher temperature divided by the temperature difference,

$$\bar{c}(T_2, T_1) = \frac{q}{T_2 - T_1}. \qquad (6.1)$$

Since the heat capacity is known to vary with temperature the true heat capacity at a given temperature may be defined by the differential expression

$$c = \frac{dq}{dT}. \qquad (6.2)$$

The heat capacity may be determined either at constant volume or constant pressure, the magnitude of the heat capacity being dependent on the mode of experimentation. In the determination of heat capacity at constant volume, none of the absorbed heat is employed in the performance of external work. Hence, the heat absorbed, q, is equal to the increase in internal energy. We may, therefore, define heat capacity at constant volume per mole of substance by the equation

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v. \qquad (6.3)$$

At constant pressure, since

$$q = \Delta E + w,$$

the heat absorbed to produce a given rise of temperature will be greater by an amount equivalent to the external work performed by the system on the surroundings. Hence, we may define the mean heat capacity at constant pressure thus:

$$\bar{c}_p = \left(\frac{q}{T_2 - T_1} \right)_p = \left(\frac{\Delta E + p\Delta v}{T_2 - T_1} \right)_p = \left(\frac{\Delta H}{T_2 - T_1} \right)_p \qquad (6.4)$$

and, for the true molecular heat capacity at constant pressure,

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p. \qquad (6.5)$$

(7) The Heat of a Chemical Reaction: Chemical reactions are in general accompanied by absorption of heat from or evolution of heat to the surroundings; they are either endothermic or exothermic. For a reaction occurring at constant volume the heat absorbed or evolved is equal to the change in internal energy, ΔE, of the system, since no external work is performed. In this particular case the change in internal energy ΔE is equal to the change in heat content, ΔH. Reactions are ordinarily conducted at constant pressure, p, and are accompanied by a volume change, Δv. The heat absorbed, q, is equal to the increase in internal energy plus the external work performed, and, thus, is equal to the change in the heat content, ΔH. Calorimetric data are, therefore, normally expressed in terms of the change in heat content. Two examples may be cited which are basic data in the calorimetry of organic compounds, the heats of formation of water and carbon dioxide at 25° C. = 298.16° K from their elementary constituents.

$$H_2(g.) + \tfrac{1}{2}O_2(g.) = H_2O(l.); \quad \Delta H^0_{298.16} = -285,795 \pm 40 \text{ int. j. per mole}$$
$$= -68,318.1 \pm 9.6 \text{ cal. per mole}$$
$$C(c., \text{graphite}) + O_2(g.) = CO_2(g.); \quad \Delta H^0_{298.16} = -393,355 \pm 46 \text{ int. j. per mole}$$
$$= -94,029.8 \pm 11.0 \text{ cal. per mole.}$$
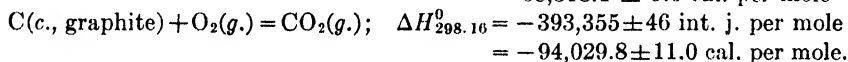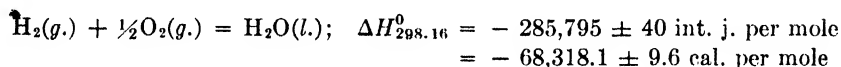
The symbols in parentheses designate the physical state of the substance: $c.$ = crystal; $l.$ = liquid; $g.$ = gas. The values expressed in calories are carried to more figures than are significant, but are so given that one may recover the value in international joules on reconversion to that unit by means of the factor 4.1833.[1]

---

[1] The data are cited from F. D. Rossini, *Chem. Rev.*, **27**, 1 (1940). Actually, the data on hydrogen refer to hydrogen which contains its natural isotopic content of HD, amounting to 0.0004 mole fraction of HDO in the resultant water. The heat of formation of ^1H_2O from $^1H_2 + O_2$ would have the value, $\Delta H^0_{298.16} = -285,793 \pm 40$ int. j./mole (Rossini, Knowlton and Johnson, *J. Res. Nat. Bur. Stand.*, **24**, 369 (1940)). The oxygen used was the normal mixture of oxygen isotopes.

As standard temperature of reference, 25° C. = 298.16° K. is usual in modern calorimetric practice.   For the reactants, the standard reference state is the pure liquid or the solid either in its stable state or in an explicitly designated state at the standard temperature and at a pressure of 1 atm.   For a gaseous reactant the standard reference state is the gas in the hypothetical state of unit fugacity (1 atm.) where the heat content is the same as that of the real gas at zero pressure.   It is convenient to indicate the standard state by a superscript zero attached to the symbol, the temperature being designated by a subscript.   Thus, in the case of the heat content, this would be written $H^0_{298.16}$.

The calorimetric quantities given in the preceding thermochemical equations may be designated the heats of formation of the two compounds, water and carbon dioxide, from their constituent elements or, since all of the substances involved are in their standard reference states, they may be termed the standard heats of formation.   This assignment involves a convention which takes account of the lack of knowledge concerning the absolute value of the heat content.   For each elementary substance in its standard reference state we assume that the heat content is zero.   With this convention the heat content of a compound is equal to the heat of formation.   Other conventions are occasionally employed.   Thus, if it be assumed that the heat content of the substance is zero in its monatomic state, then each element or compound in its molecular state would have a negative heat content numerically equal to the heat of formation of the molecule from its constituent atoms.   No change in the general utility of the thermochemical equations would result, provided the convention were applied consistently.

(8) **The Constancy of the Heat of Reaction: Hess's Law:** Since, in any process, both quantities ΔE and ΔH are dependent on the initial and final states of the system only and are independent of the path between, it follows that both the heat of reaction at constant volume and that at constant pressure, being numerically equal but opposite in sign to the increase in internal energy, ΔE, and that of heat content, ΔH, respectively, must also be defined by the initial and final states of the system independent of the path taken.   In other words the heat evolved in any chemical reaction at either constant pressure or constant volume is independent of the manner in which the reaction is achieved whether in one or many steps.   Thus, in the combustion of carbon to carbon dioxide the heat of reaction at constant pressure, $-\Delta H_1$, is equal to that for the two-stage process: (a) carbon to carbon monoxide, $-\Delta H_2$, (b) carbon monoxide to carbon dioxide, $-\Delta H_3$.   Thus, from the data of Bischowsky and Rossini,[1] applicable at a temperature of 18° C.,

$$C(c.\ diamond) + O_2(g.) = CO_2(g.) - \Delta H_1 = 94.45 \text{ kcal.}$$
$$C(c.\ diamond) + \tfrac{1}{2}O_2(g.) = CO\ (g.) - \Delta H_2 = 26.84 \text{ kcal.}$$
$$CO(g.) + \tfrac{1}{2}O_2(g.) = CO_2(g.) - \Delta H_3 = 67.61 \text{ kcal.}$$
$$-\Delta H_1 = (-\Delta H_2) + (-\Delta H_3).$$
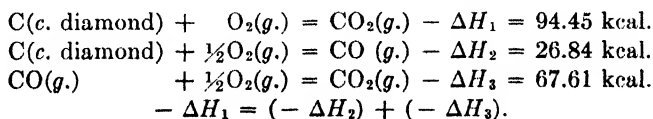
[1] F. R. Bichowsky and F. D. Rossini, Thermochemistry of Chemical Substances, Reinhold Pub. Corp., New York, 1936.

This consequence of the first law of thermodynamics, which is of great utility in the science of thermochemistry, was first enunciated by Hess in 1840, prior to the formulation of the law of conservation of energy, of which it is a special case. The law forms the theoretical basis of the classical experimental work of Thomsen and Berthelot on the thermal magnitudes of a wide variety of chemical compounds. For, the law of Hess involves as corollaries a number of useful conclusions. Thus, the heat of formation of a compound must be independent of the manner of its formation; the heat of reaction must be independent of the time consumed in the process; the heat of reaction must be equivalent to the sum of the heats of formation of the products of the reaction less the sum of the heats of formation of the initial reactants.

(9) **Heat of Reaction and Temperature: Kirchoff's Law:** The heat of reaction of a given process varies with the temperature, the mode of variation of which may be elucidated by consideration of a given process,

$$A \rightarrow B,$$

occurring at two temperatures T and $T + dT$ differing infinitesimally. For simplicity let the several processes be assumed to occur at constant volume. In the first place the reaction may be assumed to occur at temperature T whereby q calories of heat are yielded to the surroundings. The system B may now be raised from T to $T + dT$. This will require absorption of heat by the system equal to $C_v'dT$, where C_v' is the heat capacity of the system B at constant volume in the given small temperature interval. In the second place, the process may be achieved by another path. The system A may be raised from T to $T + dT$ whereby analogously the heat absorbed will be $C_v dT$. The reaction A to B may now be conducted at the temperature $T + dT$ whereby a heat evolution equal to $q + dq$ calories occurs. From the law of conservation of energy, the heat change from A at temperature T to B at temperature $T + dT$ is independent of the path by which it is achieved; otherwise, a perpetual motion machine could be realized. Hence, assigning positive values to heat absorbed by the system and negative values to heat given to the surroundings, we obtain by equating the two modes of procedure

$$- q + C_v'dT = C_v dT - (q + dq),$$

whence

$$dq = (C_v - C_v')dT$$

or

$$\frac{dq}{dT} = C_v - C_v'. \tag{9.1}$$

Since, at constant volume, q, the heat evolved in a process is equal to $- \Delta E$, we may write the equation

$$\frac{d(\Delta E)}{dT} = C_v' - C_v = \Delta C_v. \tag{9.2}$$

In a similar manner it may be shown that, operating at constant pressure instead of at constant volume,

$$\frac{d(\Delta H)}{dT} = \Delta C_p, \tag{9.3}$$

where ΔC_p represents the heat capacity at constant pressure of the products less that of the reactants. The temperature coefficient of the heat of reaction under any circumstances is therefore equal to the change in the heat capacity which the system undergoes in those circumstances. This law was first deduced by Kirchhoff [1] in 1858. It is applicable alike to chemical reactions and to all those processes such as fusion, vaporization and the like which we more usually term physical processes. More recently the applicability of the law in cases of sub-atomic nature has been demonstrated.

(10) **The Thomsen-Berthelot Principle: An Erroneous Concept of Chemical Affinity:** The idea underlying the comprehensive investigations of Thomsen (1854 onwards) and of Berthelot in the domain of thermochemistry was the assumption that the heat of reaction was a direct measure of chemical affinity. In the words of Berthelot, "every chemical change which takes place without the aid of external energy tends to the production of that system which is accompanied by the development of the maximum amount of heat." This principle is wrong. Many reasons may be adduced to prove its incorrectness. If the principle were true, only exothermal reactions could take place unless external energy were simultaneously utilized. For, endothermic reactions would indicate a negative affinity or a repulsion. The existence of endothermic reactions had, therefore, to be explained by the proponents of the theory by assumption of the operation of secondary physical factors. Thus, the spontaneous solution of many salts in water, frequently endothermal, is apparently a contradiction of the Thomsen-Berthelot principle. It was "explained" that although the net observed heat effect was negative, the positive value, due to the affinity proper, was masked by secondary thermal magnitudes due to physical changes, e.g., the change of the solid salt to the fluid condition in solution. Such assumptions, impossible of test by measurement, only served to complicate what is, as will be shown, a very simple quantity, the chemical affinity of a system. The Thomsen-Berthelot principle implied, moreover, that reactions should proceed to completion in that direction in which exothermicity was developed. This had been definitely disproved by the researches of Berthollet at the beginning of the nineteenth century; the concept of balanced actions became indispensable when the Law of Mass Action was put forward by Guldberg and Waage in 1864. Balanced actions and equilibrium involve the simultaneous occurrence of exothermal and endothermal changes at one and the same temperature.

It will emerge in the subsequent discussion that the heat of reaction is not the true thermodynamic criterion for chemical reaction. On the contrary,

[1] *Pogg. Ann.*, **103**, 454 (1858).

the change of free energy, the capacity of the system to do chemical, electrical or mechanical work, will be shown to be the correct measure of the driving force of a reaction. In certain special, but accidental, cases, the heat of reaction and the free energy of the process may be equal. In the majority of cases this will not be true. To demonstrate the correct relationship between these two magnitudes the first law of thermodynamics is insufficient. New limitations on the convertibility of energy must first be discussed and these will lead to a second law of thermodynamics. In the meantime it may be emphasized that the law. of conservation of energy gives no information as to the *direction* of energy changes. It only insists that, whatever the direction of change, no energy shall be lost or gained by the system taken as a whole.

(11) **Thermochemical Data**: Thermochemistry is concerned fundamentally with the determination of the heat changes accompanying two types of process (*a*) change of state, (*b*) chemical reaction. The important calorimetric quantities are therefore (1) heats of vaporization and sublimation, (2) heats of fusion, (3) heats of transition, (4) heats of formation together with, (5) specific heats. In multicomponent systems it is necessary also to know (1) heats of solution, (2) heats of dilution and (3) heats of interaction, for example, neutralization, in solution. A thermochemical investigation involves, in modern procedure, two types of measurement. In one there is measured the amount of chemical reaction or physical change the occurrence of which produces a specified change in a calorimeter, and in the other there is measured the quantity of electricity that produces the same change in the calorimeter. In formulating, thus, the fundamentals of thermochemical investigation Rossini[1] has pointed out that present day requirements place a heavy burden upon accuracy and precision of measurements which the great body of thermochemical data accumulated by Thomsen, Berthelot and others prior to 1900 falls far short of meeting. In the earlier work an accuracy of ± 1 kcal. would be regarded as satisfactory; today's thermodynamic requirements frequently demand a precision ten times as great.

The chemical reactions whose heats require measurement are grouped by Rossini in three classes:

1. Reactions substantially in the gaseous phase at constant pressure.
2. Reactions substantially in the liquid phase at constant pressure.
3. Reactions in a closed bomb at constant volume.

As examples of the first class, occurring in the calorimeter vessel, generally in a flame or at the surface of a catalyst, the following may be cited:

$$H_2(g.) + \tfrac{1}{2}O_2(g.) = H_2O(l.),$$
$$\tfrac{1}{2}Cl_2(g.) + \tfrac{1}{2}H_2(g.) = HCl(g.),$$
$$CH_4(g.) + 2O_2(g.) = CO_2(g.) + 2H_2O(l.),$$
$$C_2H_4(g.) + H_2(g.) = C_2H_6(g.),$$
$$O_2(g.) + S(c.) = SO_2(g.).$$
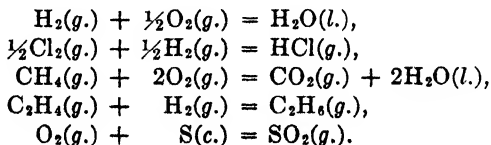
[1] F. D. Rossini, *Chem. Rev.*, **18**, 233 (1936); **27**, 1 (1940).

They include heats of combustion, of hydrogenation and of chlorination, with the last example occurring in a flame with oxygen burning in an excess of sulfur vapor, sulfur being present initially and finally in the solid state. In general, one of the reactants is maintained in excess and the amount of reaction is best determined by measuring the mass of one of the products.

As examples of the second class the following are illustrative:

$$HCl \cdot 100H_2O(l.) + NaOH \cdot 100H_2O(l.) = NaCl \cdot 201H_2O(l.),$$
$$HCl(g.) + 100H_2O(l.) = HCl \cdot 100H_2O(l.),$$
$$NaCl(c.) + 100H_2O(l.) = NaCl \cdot 100H_2O(l.),$$
$$NaCl \cdot 100H_2O(l.) + 100H_2O(l.) = NaCl \cdot 200H_2O(l.),$$
$$NaCl(aq.) + AgNO_3(aq.) = AgCl(c.) + NaNO_3(aq.),$$
$$Na(c.) + H_2O(l.) = NaOH(aq.) + \tfrac{1}{2}H_2(g.).$$
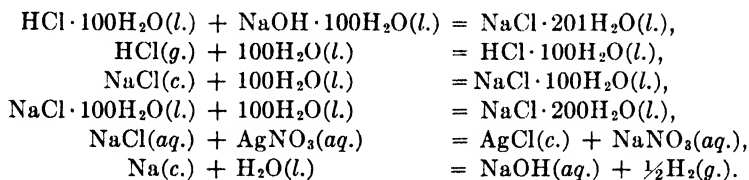
They include heats of neutralization, of solution both of gas and solid, of dilution and of chemical reaction between two solutions to form a solid precipitate, and between a solid and a liquid.

Reactions of the third class, involving bomb calorimetry in a closed bomb at constant volume and, normally, elevated pressures, are usually combustion reactions. Gases, liquids and solids may thus be treated. The method is particularly applicable to organic compounds, from the heats of combustion of which much of our knowledge of the heats of formation of organic compounds is derived. The normal combustion products in such cases are carbon dioxide and water. In commenting on the precision of such bomb calorimetric measurements, Rossini makes the following pertinent observations:

"The increasing accuracy and precision of thermochemical measurements has resulted in increasing the significance of information concerning the exact thermodynamic state of each substance participating in the chemical reaction. In former years, for example, the observed value of the heat evolved in the bomb calorimeter was taken as $-\Delta E$, the decrease in internal or intrinsic energy, for the pure reaction at 1 atmosphere. Several years ago, Washburn [1] investigated in considerable detail the reaction that actually occurs in the bomb calorimeter and showed that the value observed for the bomb reaction differs from $-\Delta E$ for the pure reaction at 1 atmosphere by amounts ranging from several hundredths to nearly 1 per cent.

"That the reaction which actually takes place in the bomb calorimeter is a complex one is made evident by considering just what the initial and final states are. The following equation illustrates the nature of the bomb process for the combustion of benzoic acid when, as is usually done, a small amount of water is initially placed in the bomb; [2] the temperature and pressure of the initial state, T_A and P_A, usually will have values between 20° and 30° C., and between 30 and 40 atmospheres, respectively; the temperature and pressure of the final state will be $T_A + \Delta T$ and $P_A - \Delta P$, where ΔT will usually have a value from 1° to 4° C. and ΔP will usually be of the order of several atmospheres:

$$C_7H_6O_2(c.) + [(30 - a)O_2 + bH_2O](g.) + [(\tfrac{1}{18} - b)H_2O + aO_2](l.) = [(7 - f)CO_2$$
$$+ (4\tfrac{5}{2} - d)O_2 + cH_2O](g.) + [(3 + \tfrac{1}{18} - e)H_2O + dO_2 + fCO_2](l.).$$
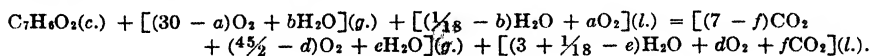
[1] E. W. Washburn, *Bur. Standards J. Res.*, **8**, 729 (1932).

[2] The presence of nitrogen in the oxygen used for the combustion further complicates the reaction through the formation of a significant amount of aqueous nitric acid:

$$\tfrac{1}{2}N_2(g.) + \tfrac{5}{4}O_2(g.) + \tfrac{1}{2}H_2O(l.) = HNO_3(aq.).$$
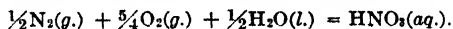
This complex actual reaction is to be compared with the simple reaction for which the thermochemical value is desired, the temperature and pressure of the reactants and products being, for example, 25° C. and 1 atmosphere:

$$C_7H_6O_2(c.) + {}^{15}_{2}O_2(g.) = 7CO_2(g.) + 3H_2O(l.).$$
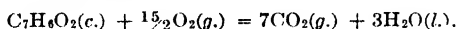
"To obtain the required thermochemical value for the simple reaction at 1 atmosphere, the observed value for the bomb reaction must be corrected with regard to the changes in internal energy with pressure of the initial oxygen and of the mixture of oxygen and carbon dioxide of the final state, the heat of solution of oxygen and carbon dioxide in water, and the heat of vaporization of water.

TABLE I

HEATS OF FORMATION OF GASEOUS HYDROCARBONS FROM SOLID CARBON (GRAPHITE) AND GASEOUS HYDROGEN AT 25° C.

Substance	Formula and State	$\Delta H^0_{298.16}$	
		Int. j. per mole	Cal. per mole
Paraffins:			
Methane............	$CH_4(g.)$	$-74,735 \pm 310$	$-17,865 \pm 74$
Ethane.......... ...	$C_2H_6(g.)$	$-84,465 \pm 450$	$-20,191 \pm 108$
Propane............	$C_3H_8(g.)$	$-103,535 \pm 520$	$-24,750 \pm 124$
n-Butane............	$C_4H_{10}(g.)$	$-124,305 \pm 640$	$-29,715 \pm 153$
Isobutane	$C_4H_{10}(g.)$	$-131,145 \pm 550$	$-31,350 \pm 132$
n-Petane......... ..	$C_5H_{12}(g.)$	$-145,325 \pm 890$	$-34,739 \pm 213$
2-Methylbutane..... .	$C_5H_{12}(g.)$	$-153,405 \pm 640$	$-36,671 \pm 153$
Tetramethylmethane...	$C_5H_{12}(g.)$	$-164,865 \pm 950$	$-39,410 \pm 227$
Monoölefins:			
Ethylene............	$C_2H_4(g.)$	$52,526 \pm 280$	$12,556 \pm 67$
Propylene	$C_3H_6(g.)$	$20,732 \pm 460$	$4,956 \pm 110$
1-Butene........	$C_4H_8(g.)$	$1,602 \pm 750$	383 ± 180
cis-2-Butene....	$C_4H_8(g.)$	$-5,806 \pm 750$	$-1,388 \pm 180$
trans-2-Butene.........	$C_4H_8(g.)$	$-9,781 \pm 750$	$-2,338 \pm 180$
"Isobutene" (2-methyl-propene).....	$C_4H_8(g.)$	$-13,407 \pm 690$	$-3,205 \pm 165$
1-Pentene............	$C_5H_{10}(g.)$	$-19,427 \pm 1260$	$-4,644 \pm 300$
cis-2-Pentene..	$C_5H_{10}(g.)$	$-26,794 \pm 1260$	$-6,405 \pm 300$
trans-2-Pentene..	$C_5H_{10}(g.)$	$-30,756 \pm 1260$	$-7,352 \pm 300$
2-Methyl-1-butene.....	$C_5H_{10}(g.)$	$-35,240 \pm 840$	$-8,424 \pm 200$
3-Methyl-1-butene.....	$C_5H_{10}(g.)$	$-27,518 \pm 750$	$-6,578 \pm 180$
2-Methyl-2-butene.....	$C_5H_{10}(g.)$	$-41,812 \pm 750$	$-9,995 \pm 180$
Diolefins:			
Allene...............	$C_3H_4(g.)$	$192,624 \pm 1090$	$46,046 \pm 260$
1, 3-Butadiene...... ..	$C_4H_6(g.)$	$112,384 \pm 1000$	$26,865 \pm 240$
1, 3-Pentadiene........	$C_5H_8(g.)$	$79,002 \pm 1260$	$18,885 \pm 300$
1, 4-Pentadiene........	$C_5H_8(g.)$	$106,946 \pm 1260$	$25,565 \pm 300$
Acetylenes:			
Acetylene........	$C_2H_2(g.)$	$226,852 \pm 980$	$54,228 \pm 235$
Methylacetylene.......	$C_3H_4(g.)$	$185,358 \pm 1000$	$44,309 \pm 240$
Dimethylacetylene.....	$C_4H_6(g.)$	$147,340 \pm 1490$	$35,221 \pm 335$

"In his comprehensive study, Washburn derived the complete and the approximate equations for correcting the heat of the bomb reaction to give the heat of the pure reaction at 1 atmosphere, and proposed certain standard states for bringing uniformity in the data of bomb calorimetry. The important variables in this connection are the volume of the bomb, the mass of substance burned, the amount of water initially placed in the bomb, and the initial pressure. Washburn's recommendations concerning the standard conditions of the bomb process, and his equations for correcting ΔE of the bomb reaction to ΔE of the simple reaction at 1 atmosphere, have been accepted by the Commission Permanente de Thermochimie de la Union Internationale de Chimie.

"In the case of the combustion of organic compounds containing sulfur or a halogen, the reaction is even more complicated than that described above. In each such combustion involving sulfur or a halogen, the investigator must determine, with an accuracy commensurable in significance with his calorimetric accuracy, just what the actual reaction is that occurs in the bomb. The observed heat effect must then be corrected by the appropriate amount necessary to give the heat of a reaction in which all the reactants and products are in definite known states."

The degree of precision which may be attained in modern calorimetric techniques is well illustrated by the data recently accumulated on the heats of formation of gaseous hydrocarbons from solid carbon and gaseous hydrogen at 25° C. The case in question represents a favorable condition for the attainment of precision because of the possibility of control using two techniques, one that of heats of combustion, from the work of Rossini and collaborators at the National Bureau of Standards, the other the heats of hydrogenation, from the work of Kistiakowsky and his collaborators at Harvard University. Data obtained from these sources during the last fifteen years on hydrocarbons containing five or less carbon atoms per molecule are presented in Table I. The data for the paraffins depend on heats of combustion alone. The data for olefins and acetylenes are derived from a combination of data on the two techniques.

Such data may be utilized, by application of Hess's Law, to obtain the heats of isomerization of saturated and unsaturated hydrocarbons. The data so obtained by Rossini, collected in Table II, exhibit excellently the reason for the precision of measurement required in modern thermochemistry.

TABLE II

HEATS OF ISOMERIZATION OF SATURATED AND UNSATURATED HYDROCARBONS

Isomerization	ΔH^0(298.16° K.) kcal. per mole	ΔH^0(0° K.) kcal. per mole
n-butane = isobutane	-1.64 ± 0.20	-1.27 ± 0.21
n-pentane = 2Me-butane	-1.93 ± 0.26	-1.43 ± 0.27
n-pentane = tetramethylmethane	-4.67 ± 0.31	-4.04 ± 0.32
1-butene = 2-cis-butene	-1.67 ± 0.12	-1.84 ± 0.12
1-butene = 2-trans-butene	-2.72 ± 0.12	-2.79 ± 0.12
1-butene = 2Me-propene	-3.59 ± 0.25	-3.85 ± 0.25
1-pentene = 3Me-1-butene	-1.93 ± 0.30	*
1-pentene = 2Me-1-butene	-3.78 ± 0.30	
1-pentene = 2Me-2-butene	-5.35 ± 0.30	

The values of ΔH^0 at $0°$ K. were calculated from data provided by Pitzer [1] for the gases in question. For graphite the present accepted value for $H^0(295.16°$ K.$) - H^0(0°$ K.$)$ is 251.9 ± 3.0 cal. per mole and for hydrogen 2023.9 ± 0.5 cal. per mole.

Tables of "best," self-consistent values for the heats of formation of chemical compounds, other than those of carbon compounds containing more than two carbon atoms, and including heats of transition, fusion, vaporization and ionization have been compiled by Bischowsky and Rossini.[2] In these tables, for the element carbon, diamond was chosen as the standard state. As a result of more recent researches,[3] it is concluded that the existence of more than one form of graphite is improbable and that there is every reason to use graphite as the reference state for carbon.

APPLICATIONS OF THE FIRST LAW TO GASES

(12) The Internal Energy of an Ideal Gas: In general, a gas may be defined by reference to two of the three variables, pressure, volume and temperature, any two of which will give the third a definite value. Since the internal energy of a substance is a function of its state at any given moment, it follows that the small change in internal energy dE of such a gas may be expressed by an equation of the form

$$dE = \frac{\partial E}{\partial T} dT + \frac{\partial E}{\partial v} dv, \tag{12.1}$$

in which case v and T are chosen as the two variables. Now $\partial E/\partial T$ is the heat taken up by one mole of gas when it is heated one degree without performing external work, for then

$$\Delta E = q. \tag{12.2}$$

This, however, is really the heat capacity at constant volume. Hence

$$\frac{\partial E}{\partial T} = C_v. \tag{12.3}$$

We may therefore write the above equation in the form

$$dE = C_v dT + \left(\frac{\partial E}{\partial v}\right) dv. \tag{12.4}$$

Hence, also, from the first law

$$dq = C_v dT + \frac{\partial E}{\partial v} dv + dw. \tag{12.5}$$

[1] K. S. Pitzer, *Chem. Rev.*, **27**, 39 (1940).

[2] F. R. Bischowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Pub. Corp., New York, 1936.

[3] P. H. Dewey and D. R. Harper, *J. Res. Nat. Bur. Standards*, **21**, 457 (1938); R. S. Jessup, *ibid.*, **21**, 475 (1938); F. D. Rossini and R. S. Jessup, *ibid.*, **21**, 491 (1938).

If, now, the temperature change be determined which accompanies the expansion of a gas in a thermally insulated system (i.e., $q = 0$), without performance of external work by the system on the surroundings (i.e., $w = 0$), such a temperature measurement will yield information relative to the change of internal energy with volume. This experiment was first carried out by Gay-Lussac and later by Joule, by allowing the gas from one vessel, I, to stream into an evacuated vessel, II, until pressure equilibrium was established in the complete system I + II. By having the system immersed in water in a calorimeter any temperature variation could be noted. The first experiments of this type led to the conclusion that dT was equal to zero. It was therefore concluded that, for such a system, since dv was positive,

$$\frac{\partial E}{\partial v} = 0. \tag{12.6}$$

It follows, therefore, that for all such gaseous systems as would give this experimental result the internal energy would be independent of the volume, dependent only on the temperature of the system.

More accurate measurements, subsequently performed by Joule and Thomson (later Lord Kelvin), established the fact that this conclusion was incorrect for all real gases, but that it was approached the more closely the more the gas approached a condition of ideality. The lower the initial pressure in vessel I, or the higher the experimental temperature T, the more nearly did dT approach zero and therefore the more nearly did $\partial E/\partial v$ approach zero.

The real thermodynamic criterion to be fulfilled by any ideal gas may be learned by a study of the experimental method employed by Joule and Thomson to determine the temperature changes accompanying an expansion of a real gas. The change from a high pressure p_1 to a lower pressure p_2 was made to occur slowly by interposing a resistance to the gas flow. A porous plug divided the region of high pressure from that of low pressure. As the gas passed through the plug under compression on the high pressure side, p_1, the volume on the low pressure side was increased. Diagrammatically this may be illustrated in Fig. 1.
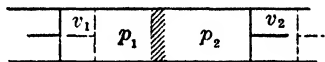
Fig. 1

The work done on the gas at high pressure p_1 for a gram mole of the gas at volume v_1 compressed through the plug is obviously p_1v_1. On the low pressure side, correspondingly, the work done by the gas on the surroundings is p_2v_2. Now if Boyle's Law be obeyed by the gas in question,

$$p_1v_1 = p_2v_2, \tag{12.7}$$

it is evident that the system as a whole has performed no external work, and $w = 0$. In a thermally insulated system q also is equal to zero. Under such circumstances

$$- C_v dT = \left(\frac{\partial E}{\partial v}\right) dv. \tag{12.8}$$

Whence, if $dT = 0$, it follows also that

$$\left(\frac{\partial E}{\partial v} \right)_T = 0. \tag{12.9}$$

Hence an ideal gas may be defined thermodynamically as a gas fulfilling two conditions,

$$(a) \quad \left(\frac{\partial E}{\partial v} \right)_T = 0, \tag{12.10}$$

$$(b) \quad pv = \text{constant}.$$

(13) **Real Gases: The Joule-Thomson Coefficient:** For real gases, in general, $p_1 v_1$ will not be equal to $p_2 v_2$. The external work performed by the system as a whole upon the surroundings will be

$$p_2 v_2 - p_1 v_1 = w. \tag{13.1}$$

According to the first law, for a process without heat absorption, a so-called *adiabatic* process,

$$\Delta E = E_2 - E_1 = -w = p_1 v_1 - p_2 v_2. \tag{13.2}$$

Hence

$$E_2 + p_2 v_2 = E_1 + p_1 v_1. \tag{13.3}$$

Since $H = E + pv$, this equation may be transformed into

$$H_2 = H_1 \tag{13.4}$$

The free expansion of a real gas occurs, therefore, not with constant internal energy E but with constant heat content H. The Joule-Thomson coefficient is therefore definable as the change in temperature produced when the gas expands at unit pressure differential and constant heat content, or mathematically

$$\mu_{\text{J.T.}} = \left(\frac{\partial T}{\partial p} \right)_H . \tag{13.5}$$

The Joule-Thomson coefficient for a number of gases under stated conditions is given in the following table. Comprehensive data for air, helium, argon, carbon dioxide and mixtures of these gases have been published by Roebuck and his collaborators.[1]

Now since in the free expansion of real gases, $H = E + pv$ is constant, i.e., $dH = d(E + pv) = 0$, and since H is also a single-valued function of any two of the variables, p, v and T, that is,

$$dH = \left(\frac{\partial H}{\partial T} \right)_p dT + \left(\frac{\partial H}{\partial p} \right)_T dp, \tag{13.6}$$

[1] J. R. Roebuck, *Proc. Am. Acad. Arts Sci.*, **60**, 537 (1925); **64**, 287 (1930); J. R. Roebuck and H. Osterberg, *Phys. Rev.*, **43**, 60 (1933); **45**, 322 (1934); *J. Chem. Phys.*, **8**, 627 (1940); J. R. Roebuck and T. A.Murrell, *Phys. Rev.*, **55**, 240 (1939).

TABLE III

JOULE-THOMSON COEFFICIENTS

Gas	$t°$ C.	$\mu_{J.T.}$ at Pressures				
		0–6	2	10	15	40 atm.
Hydrogen	6.8	-0.030^a				
	90.1	-0.044^a				
Carbon Dioxide	0	1.35^a				1.46^c
	20	1.14^a	1.21^b	1.31^b	1.37^b	1.20^c
	40	0.96^a				1.04^c
	100	0.62^a				
		$P = 0$	25	50	100	150 Kg./cm.^{2}
Air^d	-55	0.44	0.40	0.3	0.28	0.18
	0.6	0.27	0.25	0.24	0.19	0.16
	49	0.20	0.18	0.17	0.15	0.12
	150	0.09	0.09	0.07	0.06	0.05
	250	0.02	0.02	0.02	0.01	0.01
		$P = 1$	4.5	6.4 m. Hg		
Air^c	0	0.399	0.378	0.359		
	50	0.298	0.278	0.270		
	100	0.224	0.210	0.213		

[a] Joule-Thomson.

[b] Natanson, *Wied. Ann.* **31**, 502 (1887).

[c] Kester, *Phys. Rev.*, **21**, 260 (1905).

[d] Noell, *Forsch. Arbeiten* No. 184 (1916).

[e] Hoxton, *Phys. Rev.*, **13**, 438 (1919).

it follows that, since $dH = 0$,

$$\frac{dT}{dp} = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{C_p}. \tag{13.7}$$

In other words the magnitude of the Joule-Thomson coefficient is determined by the variation in the quantity H with pressure at constant temperature since C_p is a definite numerical quantity.

The variation of H with pressure at constant temperature is determined by the respective variations of E and pv of which the quantity H is composed.

$$\left(\frac{\partial H}{\partial p}\right)_T = \left(\frac{\partial E}{\partial p}\right)_T + \left(\frac{\partial(pv)}{\partial p}\right)_T. \tag{13.8}$$

Since

$$\left(\frac{\partial E}{\partial p}\right)_T = \left(\frac{\partial E}{\partial v}\right)_T \left(\frac{\partial v}{\partial p}\right)_T, \tag{13.9}$$

it follows, for the Joule-Thomson coefficient, that

$$\mu_{\text{J.T.}} = \left(\frac{\partial T}{\partial p}\right)_H = -\frac{\left(\dfrac{\partial E}{\partial v}\right)_T \left(\dfrac{\partial v}{\partial p}\right)_T}{C_p} - \frac{\left(\dfrac{\partial (pv)}{\partial p}\right)_T}{C_p}. \tag{13.10}$$

All of these quantities, except $(\partial E/\partial v)_T$, can readily be measured experimentally. These measurements therefore offer a method of obtaining the value of $(\partial E/\partial v)_T$ for a real gas. It is thus found always to have a positive value for such gases. The variation of volume with pressure, $(\partial v/\partial p)_T$, is always negative so that the first term in equation (13.10) is always positive. The variation of the pressure-volume product with pressure is dependent on both the pressure range and the temperature. At ordinary temperatures and for moderate pressures the value of $(\partial(pv)/\partial p)_T$ in the second term of equation (13.10), is negative for all gases except hydrogen and helium for which gases the product increases with pressure. Hence, it follows that, for all gases except hydrogen and helium, the Joule-Thomson coefficient will be positive at ordinary temperatures, in agreement with experimental fact. For hydrogen and helium, at ordinary temperatures, experiment shows that $(\partial T/\partial p)_H$ is negative, from which it may be concluded that, in the case of these two gases, the negative influence of the second term in equation (13.10) is greater than the positive influence of the first term.

The variation of H with pressure at constant temperature may also be examined for a gas obeying van der Waals's equation. The usual form of the equation, per mole of gas,

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \tag{13.11}$$

may be rearranged to give

$$pv = RT + bp - a/v + ab/v^2. \tag{13.12}$$

Substituting RT/p for v in the last two terms yields

$$pv = RT + (b - a/RT)p + (ab/(RT)^2)p^2. \tag{13.13}$$

Neglecting the last term on the right of the equation, and, therefore, for moderate pressures, it follows that

$$(\partial(pv)/\partial p)_T = b - a/RT. \tag{13.14}$$

Since the term a/v^2 is an internal pressure or attraction which must be overcome

when the gas expands, the energy supplied to the gas in expansion from volume v_1 to volume v_2 is given by the expression

$$\int_{v_1}^{v_2} \frac{a}{v^2}\, dv = \frac{a}{v_1} - \frac{a}{v_2}. \tag{13.15}$$

The energy of a gas may therefore be expressed by the equation,

$$E = E_0 - \frac{a}{v}, \tag{13.16}$$

where E_0 is the energy at infinite volume. Substituting RT/p for v and differentiating with respect to pressure, it follows that

$$(\partial E/\partial p)_T = -a/RT. \tag{13.17}$$

It follows therefore that, since $(\partial H/\partial p)_T = (\partial E/\partial p)_T + (\partial(pv)/\partial p)_T$, for a gas obeying van der Waals's equation, and at moderate pressures,

$$(\partial H/\partial p)_T = b - 2a/RT \tag{13.18}$$

and the Joule-Thomson coefficient in equation (13.7) becomes

$$\mu_{\text{J.T.}} = \left(\frac{\partial T}{\partial p}\right)_H = \frac{\dfrac{2a}{RT} - b}{C_p}. \tag{13.19}$$

For such a gas there is obviously a temperature, T_i, such that the coefficient becomes zero, above which it is negative and below which it is positive. This inversion temperature is given by the expression

$$T_i = \frac{2a}{Rb}. \tag{13.20}$$

All gases, with the exception of hydrogen, helium and argon are below their inversion temperature when at room temperature. The inversion temperature of hydrogen is approximately $-80°$ C. The inversion temperature is, however, dependent on the operating pressure as is obvious from the nature of the approximations involved in the above discussion and the data of Roebuck and Osterberg for argon cited in Table III.

<div align="center">

TABLE III

INVERSION TEMPERATURES FOR ARGON

</div>

$p =$	200	180	140	100	60	Atm.
$t_i =$	-119.6	-122.6	-128.3	-137.6	-146.2	$°$ C.

Rose-Innes has shown that the experimental measurements of Joule and Thomson were representable by an empirical equation conforming to that

deduced using van der Waals's equation for the gas. The empirical equation has the form

$$\frac{dT}{dp} = \frac{a}{T} + b, \tag{13.21}$$

where the constants a and b are characteristic empirical constants for each gas. For air and carbon dioxide both constants are positive in sign. For hydrogen b was negative. In this last case evaluation of the constants $a = 64.1$, $b = -0.331$ indicated that at $T = 194°$ K. or $-79°$ C. the quantity dT/dp became zero. Below this temperature, the Joule-Thomson coefficient is positive, that is, cooling is produced in hydrogen below this temperature. This is in agreement with experimental investigations of Olszewski who showed that below 80° C. hydrogen could be cooled by expansion. All the common gases, other than hydrogen, helium and argon probably show inversion points at temperatures above ordinary room temperatures.

Joule and Thomson found that the Joule-Thomson coefficient varied inversely as the square of the absolute temperature

$$\mu_{\text{J.T.}} = \frac{a}{T^2}. \tag{13.22}$$

This indicates that the lower the temperature, the greater the cooling effect produced per unit pressure gradient, a conclusion which has been experimentally verified in many cases.

The influence of pressure on the magnitude of the coefficient has been studied for oxygen at 0° C. over a considerable pressure range by Vogel.[1] The cooling effect decreased from 0.260° per atm. pressure gradient at 20 atm. pressure to 0.139° at 160 atm. pressure. Over a more limited pressure range Hoxton[2] has studied the variation in the coefficient for air. He finds also a diminution of the coefficient with increasing pressure at constant temperature, the combined effects of pressure and temperature being representable by an empirical equation

$$\mu_{\text{J.T.}} = -0.1975 + \frac{138}{T} - \frac{319P}{T^2}. \tag{13.23}$$

The Joule-Thomson effect is made use of practically for the liquefaction of gases by the so-called Linde-Hampson process. The gas cooled by expansion is utilized to pre-cool the compressed gas passing through the plug. A lower temperature is thereby produced in the gas upon expansion. The cooling is thus made cumulative until finally a temperature is attained at which liquefaction occurs. The efficiency of such a process may be calculated from the known data on the heat capacities of the gases at the two pressures, the Joule-Thomson coefficient, the boiling point and the heat of vaporization

[1] Thesis, München, 1910.
[2] *Phys. Rev.*, **13**, 438 (1919).

of the liquefied gas, when it is remembered that the heat content of the system undergoes no change.

(14) **The Relation between C_p and C_v:** It has been shown that the quantities C_p and C_v are defined by equations (6.5) and (6.3)

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p, \tag{6.5}$$

$$C_v = \left(\frac{\partial E}{\partial T} \right)_v. \tag{6.3}$$

Hence

$$C_p - C_v = \left(\frac{\partial H}{\partial T} \right)_p - \left(\frac{\partial E}{\partial T} \right)_v \tag{14.1}$$

$$= \left(\frac{\partial (E + pv)}{\partial T} \right)_p - \left(\frac{\partial E}{\partial T} \right)_v$$

$$= \left(\frac{\partial E}{\partial T} \right)_p + p \left(\frac{\partial v}{\partial T} \right)_p - \left(\frac{\partial E}{\partial T} \right)_v. \tag{14.2}$$

Now

$$dE = \left(\frac{\partial E}{\partial T} \right)_v dT + \left(\frac{\partial E}{\partial v} \right)_T dv. \tag{14.3}$$

Hence

$$\left(\frac{\partial E}{\partial T} \right)_p = \left(\frac{\partial E}{\partial T} \right)_v + \left(\frac{\partial E}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_p$$

or

$$C_p - C_v = \left(\frac{\partial E}{\partial T} \right)_v + \left(\frac{\partial E}{\partial v} \right)_T \left(\frac{\partial v}{\partial T} \right)_p + p \left(\frac{\partial v}{\partial T} \right)_p - \left(\frac{\partial E}{\partial T} \right)_v$$

$$= \left[p + \left(\frac{\partial E}{\partial v} \right)_T \right] \left(\frac{\partial v}{\partial T} \right)_p. \tag{14.4}$$

For an ideal gas it has been shown that

$$\left(\frac{\partial E}{\partial v} \right)_T = 0. \tag{12.10}$$

Hence, for such gases

$$C_p - C_v = p \left(\frac{\partial v}{\partial T} \right)_p. \tag{14.5}$$

Employing the equation of state for one mole of an ideal gas,

$$pv = RT,$$

it follows that

$$\left(\frac{\partial v}{\partial T} \right)_p = \frac{R}{p}.$$

Hence, for such gases

$$C_p - C_v = R. \qquad (14.6)$$

(15) **Isothermal Expansion of an Ideal Gas:** From the first law of thermodynamics,

$$\Delta E = q - w,$$

it has been shown that ΔE is independent of volume change for an ideal gas. Hence, in the expansion of such a gas

$$q = w. \qquad (15.1)$$

For an infinitesimal volume change dv at pressure p

$$dq = pdv. \qquad (15.2)$$

For a finite volume change, v_1 to v_2,

$$q = \int_{v_1}^{v_2} pdv. \qquad (15.3)$$

Assuming for 1 mole of gas that $pv = RT$, it follows that

$$q = \int_{v_1}^{v_2} RT\frac{dv}{v} = RT\ln\frac{v_2}{v_1}. \qquad (15.4)$$

For an ideal gas we may also put $p_1v_1 = p_2v_2$, where p_1 and p_2 are the pressures concerned. The heat absorbed in the isothermal expansion becomes therefore

$$q = RT\ln\frac{p_1}{p_2}. \qquad (15.5)$$

(16) **Adiabatic Expansion of an Ideal Gas:** In this case, since the process is adiabatic, $q = 0$. Hence

$$\Delta E = -w = -p\Delta v. \qquad (16.1)$$

Since external work is done by the system on the surroundings, the temperature of the gas must fall. The magnitude of the decrease in temperature may be determined from equation (12.5) where $q = 0$ and $\partial E/\partial v = 0$ for an ideal gas,

$$C_v dT = -pdv, \qquad (16.2)$$

whence on integration

$$C_v(T_1 - T_2) = \int_{v_1}^{v_2} pdv \qquad (16.3)$$

Alternatively, for one mole of gas,

$$C_v\frac{dT}{T} = -R\frac{dv}{v} \qquad (16.4)$$

or
$$C_v d \ln T = - R d \ln v \qquad (16.5)$$

or
$$C_v \ln \frac{T_2}{T_1} = R \ln \frac{v_1}{v_2} \cdot \qquad (16.6)$$

Now, since $C_p - C_v = R$, and putting $C_p/C_v = \gamma$,

$$\ln \frac{T_2}{T_1} = \frac{R}{C_v} \ln \frac{v_1}{v_2}, \qquad (16.7)$$

$$\ln \frac{T_2}{T_1} = (\gamma - 1) \ln \frac{v_1}{v_2} \qquad (16.8)$$

or
$$T_1 v_1^{\gamma-1} = T_2 v_2^{\gamma-1}. \qquad (16.9)$$

Since $p_1 v_1 = R T_1$ and $p_2 v_2 = R T_2$, it follows that

$$p_1 v_1^\gamma = p_2 v_2^\gamma \qquad (16.10)$$

or
$$p_1^{1-\gamma} T_1^\gamma = p_2^{1-\gamma} T_2^\gamma. \qquad (16.11)$$

(17) **Cyclic Processes**: A system which, upon completion of a change or series of changes, is in its original state is said to have completed a cycle. The whole process is known as a cyclic process. Since E is a single-valued function of its variables, dependent, therefore, only on the state of the system, independent of past history, it follows from the first law that, for every cyclic process,

$$\Delta E = 0 = q - w. \qquad (17.1)$$

If conducted at constant temperature the cycle is known as an isothermal cycle.

The cyclic process forms a useful method of studying the variation of matter when subjected to variations of energy content. The most celebrated of such cyclic processes is known as the Carnot Cycle.

(18) **The Carnot Cycle**: This cycle comprises a four-stage process to which an ideal gas may be submitted. It was employed by Carnot to demonstrate the work available from a process of heat transfer. The cycle consists of four successive processes: (*a*) an isothermal expansion, (*b*) an adiabatic expansion, (*c*) an isothermal compression at the lower temperature produced in the previous adiabatic expansion and (*d*) an adiabatic compression whereby the ideal gas is restored to its original temperature, pressure and volume. The accompanying diagram represents the p–v relationships in such a cycle starting at the state represented by A at temperature T_2, with the sequence of changes already detailed carrying the gas through states represented by the lines (*a*) *AB*, (*b*) *BC*. (*c*) *CD* and (*d*) *DA*.

The lines AB and CD represent the two isothermals, at the temperatures T_2 and T_1 ($T_2 > T_1$). The lines BC and DA represent the two adiabatics.
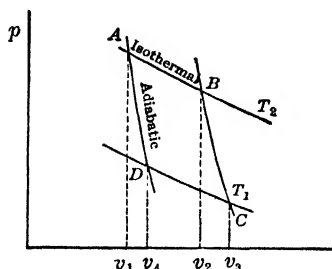
FIG. 2

Let the respective p, v, T magnitudes be for A, p_1, v_1, T_2, for B, p_2, v_2, T_2, for C, p_3, v_3, T_1 and for D, p_4, v_4, T_1.

We may follow the changes occurring in the several stages thus:

Stage I. The gas expands isothermally from A to B at temperature T_2. Heat is absorbed equal in amount to the work done by the system on the surroundings, since, for an ideal gas, the change in internal energy is zero.

$$q_2 = w_1 = RT_2 \ln \frac{v_2}{v_1}. \tag{18.1}$$

Stage II. The gas expands adiabatically from B to C. The heat absorbed is zero; hence the work done is

$$w_2 = C_v(T_2 - T_1), \tag{18.2}$$

where $T_2 - T_1$ is the change in temperature resulting from the adiabatic expansion.

Stage III. The gas is compressed isothermally from C to D in a reservoir at T_1, whereby the heat q_1 is given up to the surroundings in amount equal to the work of compression

$$q_1 = w_3 = RT_1 \ln \frac{v_3}{v_4}. \tag{18.3}$$

Stage IV. The gas is compressed adiabatically from D to A. The work done on the gas is

$$w_4 = C_v(T_2 - T_1), \tag{18.4}$$

where $T_2 - T_1$ is the increase in temperature produced by the adiabatic compression.

The net heat absorbed by the gas in the whole cycle is, therefore,

$$q = q_2 - q_1 = RT_2 \ln \frac{v_2}{v_1} - RT_1 \ln \frac{v_3}{v_4}. \tag{18.5}$$

From our knowledge of adiabatic expansions of an ideal gas we know that in the two adiabatic processes considered

$$C_v \ln \frac{T_2}{T_1} = R \ln \frac{v_3}{v_2} \quad \text{(Stage II)} \tag{16.6}$$

and

$$C_v \ln \frac{T_2}{T_1} = R \ln \frac{v_4}{v_1} \quad \text{(Stage IV)}. \tag{16.6}$$

Hence

$$\frac{v_3}{v_2} = \frac{v_4}{v_1} \quad \text{or} \quad \frac{v_2}{v_1} = \frac{v_3}{v_4}. \tag{18.6}$$

Hence

$$q = q_2 - q_1 = R(T_2 - T_1) \ln \frac{v_2}{v_1}. \tag{18.7}$$

Similarly, the work done by the gas,

$$w = w_1 + w_2 - w_3 - w_4 = R(T_2 - T_1) \ln \frac{v_2}{v_1}, \tag{18.8}$$

which satisfies the condition for a cyclic process, $w = q$. The work done may now be compared with the quantity of heat q_2 absorbed at the higher temperature T_2. From equations (18.8) and (18.1) it follows that,

$$w = q_2 \frac{T_2 - T_1}{T_2}. \tag{18.9}$$

It is therefore evident that, in the cycle, a quantity of heat q_2 has been absorbed from the surroundings at a temperature T_2 and partly transformed into the work w, the remainder q_1 being given up to the surroundings when at a lower temperature T_1. The work obtained in such a process is a definite fraction, $(T_2 - T_1)/T_2$, of the absorbed heat. We may now proceed to an examination of the question whether this quantity of work w represents the maximum amount of work possible in such a heat transfer; whether also the same fraction would be obtainable were the system employed not an ideal gas. The answer to such problems leads us into the realm of the direction of energy change and the restrictions upon the interconvertibility of energy which experience has embodied in the second law of thermodynamics.

The Second Law of Thermodynamics

An inquiry into the direction of change which a given system will undergo may well begin with an inquiry into some well-known examples of direction of change and the characteristics which such processes possess.

(19) **Reversible and Irreversible Processes:** We are quite familiar with a variety of processes, both physical and chemical, which will proceed of themselves, or as we so designate them, spontaneously occurring processes. Heat is spontaneously transferred from a hot to a cold body either by contact or by radiation. Uniformity of temperature throughout the system will eventually result. With a concentrated solution in contact with a more dilute solution, diffusion of the solute will spontaneously occur and continue until a uniform concentration results. Gases permeate a vacuum. Similarly, the inter-diffu-

sion of two gases when brought together is another familiar phenomenon. An electric current will flow along a conductor when differences of potential manifest themselves, just as water will flow from a region of higher level to a lower level until a uniform level is secured throughout the system. Many chemical reactions occur spontaneously; ammonia and hydrogen chloride gas at ordinary temperatures when brought into contact will react to yield solid ammonium chloride. All such processes proceed of themselves; *they are also, of themselves, irreversible.* All are tending to a state of greater stability. The *velocity* with which such a position of greater stability is approached may vary widely. The *trend* in that direction is definite and cannot be reversed by the system of itself. Only by the employment of external agencies can the direction of such processes be reversed. The final state which such a system attains is spoken of as a state of equilibrium. A system in such a state is characterized by the uniformity in the intensity of all its forms of energy. In reaching this finality many halting places may occur. The system in such case is in a state of metastable equilibrium. Thus, for example, hydrogen and oxygen at room temperatures are only apparently in equilibrium. In reality they are in partial or metastable equilibrium, as the introduction of a small amount of platinum black into the system would demonstrate. Water would result from the interaction of the gases. But, in no conceivable manner, without the intervention of external agencies, could the process be expected to reverse itself, to proceed from the water stage back to the state of the gas mixture. We might generalize such observations in the conclusion that: *spontaneously occurring processes are irreversible.*

Let us now examine the conditions under which we must operate in order to approximate to reversibility in the conduct of a process. The direction which any energy change takes is determined by the relative magnitudes of the intensity factors of the energy of the system and of its surroundings. At equilibrium the intensities of all the forms of energy are uniform. An infinitesimal variation in any one intensity factor will produce a change in that direction which will tend towards uniformity.

Imagine a pure liquid in equilibrium with its saturated vapor enclosed in a cylinder fitted with a piston the pressure upon which may be delicately adjusted. Let the apparatus be at constant temperature in a large reservoir from which the system may withdraw heat or to which it may give up heat. The piston will be stationary when the pressure on the piston is exactly equal to the pressure of the saturated vapor at the given temperature. Any displacement of the pressure on the piston, no matter how small, will cause a change to take place in the system, liquid-vapor. If the pressure on the piston be diminished infinitesimally, the piston will rise. The volume occupied by the saturated vapor will increase and hence a little of the liquid will evaporate to produce the saturation pressure. In doing this, heat will be abstracted from the reservoir. In this way, a process may be continuously operated, namely, the change from liquid to saturated vapor at a given temperature. The process will be exceedingly slow since the difference in the intensity factors is, under

assumption, infinitesimally small. The process may also be reversed. Imagine a pressure on the piston infinitesimally greater than the saturated vapor pressure. The piston will, under such circumstances, compress the saturated vapor into a smaller volume, the supersaturation of the vapor which would thereby result being overcome by condensation of some of the vapor. By this reversal of the process vapor may be converted to liquid. Heat will be given up to the surrounding reservoir.

The energy expended in two such processes as we have just outlined may now be computed. Let the saturated vapor pressure at the constant temperature T be equal to p. In the first case let the pressure on the piston be $p - dp$, i.e., infinitesimally smaller than p. Let the volume change, dv, be infinitesimally small. The work expended by the system on the surroundings will be

$$(p - dp)dv = pdv - dp \cdot dv. \tag{19.1}$$

If dp and dv are infinitesimally small, the second factor $dp \cdot dv$ is an infinitesimal of the second order, negligible in comparison with pdv. Substantially therefore, the work done is pdv. In the second process considered, that of compression, the pressure on the piston must be slightly greater than p, say $p + dp$. Let the system, after the expansion, be compressed by such a pressure through a volume decrease $- dv$. The work done on the system will be

$$- (p + dp)dv = - (pdv + dp \cdot dv) \tag{19.2}$$

or $- pdv$ when second order infinitesimals are neglected. The system is now in its original condition, the heat changes paralleling the two processes having occurred and being demonstrably equal and opposite, provided that no accidental and irreversible processes have simultaneously occurred. For this, it is necessary to assume that the piston shall be both weightless and frictionless since otherwise irreversible changes, e.g., those due to friction, would doubtless have occurred. Such a process represents an ideal to which all naturally occurring processes may approximate without ever realizing. Such an ideal process, however, though not actually realizable, is, nevertheless, conceivable. From the mental conception and its consequences, definite conclusions may be reached. Such an ideal process is characterized by its complete reversibility in contrast to actual processes which will always contain elements of irreversibility to a greater or less degree. In the ideal process, all of the stages of the process may be repeated in inverse order in point of time, the net expenditure of energy by all the mechanical forces involved being zero on completion of the whole process.

One other example, involving another form of energy, may be cited to illustrate the concept of reversible processes and to show the approximation to the ideal process which may be achieved by a real process. The lead storage battery, when discharging, yields current at approximately 2 volts. When the battery is discharged the process may be reversed by supplying current to the battery. As normally operated, the process of discharge and charge is accom-

panied by a number of irreversible phenomena, diffusion of electrolyte, heat losses and the like. The discharge of the battery may, however, be secured under conditions approximating to the ideal reversible process by opposing to the flow of current from the battery a current at a potential infinitesimally smaller than that of the battery. Under such circumstances current would be drawn from the battery in infinitesimally small amounts at minute speed and the factors of irreversibility in the process would be reduced to a minimum. At any moment by increasing the opposing potential infinitesimally beyond that of the battery the direction of current flow would be reversed, the battery would begin to charge. Furthermore, as in the previous case, the energy expenditure for any infinitesimal change in one direction will be exactly equal numerically to that expended in the reverse case. This type of reversible process is approximately obtained in the Poggendorff method of measurement of the electromotive forces of galvanic elements. The unknown potential is measured by opposing to it a potential of known magnitude, equality of potential being indicated by zero displacement of a galvanometer suitably placed in the electrical circuit. With such a system, very minute quantities of current could be drawn from a galvanic element and the actual conditions of energy change would approximate very closely to the ideal reversible conditions.

(20) **Maximum Work:** It is characteristic of such ideal reversible processes that the external work performed by the system undergoing change is the maximum amount of work that the system is capable of accomplishing. It is very evident that, if all irreversible effects could be eliminated from a process, the efficiency of the process should be a maximum. This is actually true. It may be made the more evident from a reconsideration of some ideal processes. In the isothermal expansion of an ideal gas through an infinitesimal volume change, dv, the work done is pdv. The magnitude of this quantity is obviously dependent on the opposing pressure p. When p is zero, expansion against a vacuum, the work done is zero. As p is increased the work done, pdv, also increases. The value attains a maximum when the driving pressure of the gas is infinitesimally greater than the opposing pressure. For, if these two pressures are equal, no volume change can occur; and if the opposing pressure be infinitesimally greater than the gas pressure, contraction in volume of the system will result. The maximum external work is therefore done when driving and opposing forces differ infinitesimally. This condition is, we have seen, that demanded by an ideal reversible process at all stages of its operation. The external work performed in a reversible process is therefore the maximum work available in the conduct of the process. In the expansion process just discussed, the reversible and maximum work, W_r, done by the system is therefore

$$W_r = pdv. \tag{20.1}$$

For a finite volume change conducted isothermally and reversibly

$$W_r = \int_{v_1}^{v_2} pdv, \qquad . \tag{20.2}$$

which, as we have previously shown for an ideal gas, is

$$W_r = RT \ln \frac{v_2}{v_1} = RT \ln \frac{p_1}{p_2} \cdot \qquad (20.3)$$

A little consideration will show also that the work done on the surroundings in an adiabatic expansion, as formulated in the equations of Section 16 and utilized in Stages II and IV of the Carnot cycle (Section 18), also gives the maximum work available from the process. We may therefore conclude that in the complete cyclic process already considered, the Carnot cycle, all the operations being conducted reversibly, the external work performed is the maximum work that can be accomplished in that cycle of operations. The relationship given by the Carnot cycle may therefore be written

$$W_{r,c} = q_2 \frac{T_2 - T_1}{T_2}, \qquad (20.4)$$

the work, $W_{r,c}$, of the reversible cycle, done by the system in the transfer of heat q_2 from temperature T_2 to T_1 representing the maximum amount of work obtainable in an ideally conducted process. All real processes would yield a smaller amount of external work.

Furthermore, in a process consisting of a transfer of heat it may be shown that the fraction converted into useful work is independent of the mechanism whereby heat is transferred, provided that this mechanism is reversible. For, let us assume a reversible cycle producing an amount of work $W'_{r,c}$ greater than $W_{r,c}$ obtained in the Carnot cycle previously considered. In such case a quantity of heat, q_2, will be taken from the reservoir at T_2 and a quantity of heat q_1' ($< q_1$) be given to the reservoir at T_1, whereby the relationship is obtained,

$$q_2 - q_1' = W'_{r,c}. \qquad (20.5)$$

Then, by employing the Carnot cycle for an ideal gas, in the reverse direction from that previously considered, a quantity of heat q_1 can be taken from the reservoir at T_1 and with the aid of a portion of the work $W'_{r,c}$, actually the quantity $W_{r,c}$, an amount of heat q_2 can be put back into the reservoir at temperature T_2. As a result of this compound cycle the only change in the system as a whole is that a quantity of heat $q_1 - q_1'$ has been taken from a reservoir at T_1 and converted into useful work, $W'_{r,c} - W_{r,c}$, without causing any other permanent changes in the system as a whole. Experience teaches that such a machine is impossible. It is not in contradiction of the first law of thermodynamics, since heat energy is consumed in the production of work.

(21) **The Second Law of Thermodynamics:** The possibility of constructing such a machine is denied by the Second Law of Thermodynamics, based upon the experience of man in the search for such a machine. Were such a machine possible, whereby heat could be continuously converted into work without compensation, an even more wonderful perpetual motion than that denied by

the first law would be possible. It would be possible continuously to utilize the large heat reservoirs of our environment to supply the motive power of our universe. It would be possible, for example, to drive a ship with the store of heat energy available in the ocean in which the ship was placed. Such a perpetual motion machine, which Ostwald has called a perpetual motion machine of the second kind, is specifically denied by experience and has resulted in the enunciation of the Second Law of Thermodynamics. One possible formulation of the law is: for useful work to be produced from heat without compensation, a transfer of heat from a higher to a lower temperature is demanded. The fraction of heat converted into work is given by equation (20.4), and this is the maximum work available. It is therefore evident that whatever the reversible mechanism used for the heat transfer from a higher to a lower temperature reservoir the maximum work available is a constant.

With an engine working in a heat reservoir at its own temperature it is obvious that $T_2 - T_1$ and, therefore, $W_{r,c}$ must be zero. It follows also that the work done in an isothermal reversible cycle is equal to zero, since the internal energy does not change, $\Delta E = 0$, and, by the second law, the heat of the isothermal environment cannot be converted into useful work.

(22) **Reversible Cycles and Carnot Cycles:** Any reversible cycle can be shown to be equivalent to a sum of Carnot cycles. In the accompanying diagram, Fig. 3, let the continuous lines AB, BA represent the path of a reversible cycle. It is evident that the path A to B may be traversed by a number of isothermals and adiabatics as shown. Similarly the return path may be so traversed. The broken line path A to B approximates the more closely to the continuous curve AB the more minute the isothermal and adiabatic changes become. The same holds true for the reverse path BA. By prolonging the isothermals back into the enclosed portion of the diagram it is evident that the area ABA may be regarded as made up of a large number of infinitely small Carnot cycles actually equal to the reversible cycle under consideration. In the summation, all those portions of the small isothermals within the actual cycle will be traversed once in the one direction, once in the reverse direction so that the net resultant of such sections is zero. The properties of any reversible cycle will therefore be equal to the summation of the properties of all the Carnot cycles of which it may be regarded as composed.
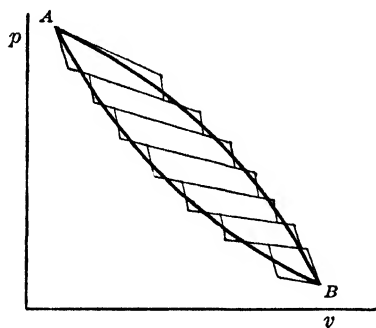
Fig 3

(23) **The Concept of Entropy:** In the discussion of the Carnot cycle and in the generalization of the conclusions therefrom for any reversible cycle, we saw that the heat q_2 taken isothermally from a reservoir at T_2 was related to the heat q_1 given up to the reservoir at T_1 and to the maximum work $W_{r,c}$ by

means of the relation

$$q_2 - q_1 = W_{r,c} = \frac{T_2 - T_1}{T_2} q_2. \qquad (23.1)$$

It follows, therefore, for any reversible cycle, that

$$\frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} \qquad (23.2)$$

or that

$$\frac{q_1}{T_1} = \frac{q_2}{T_2}. \qquad (23.3)$$

If the cycle is not reversible, if any irreversible effects are present resulting in the dissipation of heat, it is evident that the work done must be less than $[(T_2 - T_1)/T_2]q_2$. Under such circumstances

$$\frac{q_2 - q_1}{q_2} < \frac{T_2 - T_1}{T_2} \qquad (23.4)$$

or

$$\frac{q_2}{T_2} < \frac{q_1}{T_1}. \qquad (23.5)$$

Regarded from the standpoint of the machine conducting the Carnot cycle the above expression for the equality of q_1/T_1 and of q_2/T_2 may be rearranged so that $+ q$ represents heat absorbed by the machine, as is conventional in thermodynamics. In such circumstance we have for the Carnot cycle

$$\frac{- q_1}{T_1} = \frac{q_2}{T_2} \qquad (23.6)$$

or

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0. \qquad (23.7)$$

Similarly for an irreversible process

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} < 0, \qquad (23.8)$$

where again q_1 and q_2 are the heats *absorbed by the machine* at the two temperatures.

For each individual Carnot cycle into which a reversible cycle may be divided, the relationship (23.7) will hold. When the isothermal and adiabatic changes of each Carnot cycle are infinitesimally small, the summation of the Carnot cycles is equal to the reversible cycle ABA in the preceding diagram. For the Carnot cycles, therefore,

$$\sum \frac{q}{T} = 0. \qquad (23.9)$$

When the changes are infinitesimal, correspondingly,

$$\oint \frac{dq}{T} = 0, \tag{23.10}$$

where the circle through the integral implies integration over the whole cycle. This expression is applicable to any reversible cycle irrespective of its nature or the path by which it is achieved provided that this be a reversible path. In the preceding figure, where the cycle is achieved in two stages A to B and B to A, it is evident that

$$\oint \frac{dq}{T} = \int_A^B \frac{dq}{T} + \int_B^A \frac{dq}{T} = 0. \tag{23.11}$$

Both of these integrals are evidently independent of the path taken from A to B or conversely from B to A. Both are therefore determined by the properties of the initial and final states A and B. They are therefore evidently equal to the change in some single-valued function of the variables of the states A and B of the system. This relationship may be expressed by the equation,

$$\Delta S = S_B - S_A = \int_A^B \frac{dq}{T}, \tag{23.12}$$

whence it follows that

$$dS = \frac{dq}{T} \cdot \tag{23.13}$$

These expressions give us a definition of the entropy of a system. The increase ΔS in the entropy, S, of a reversible process is the integral of all the heat changes which the system undergoes in passing from state A to state B, each heat change to be divided by the absolute temperature at which it occurred. The concept of entropy received this definition from Clausius who emphasized its importance in the formulation of the statement of the second law of energetics, its dependence on the state of the system and its independence of the path by which the state is achieved.

(24) **Entropy Change in an Isolated System:** Consider a system in which the component elements have internal energies respectively E_A, E_B, E_C, $\cdots$, pressures p_A, p_B, p_C, $\cdots$, volumes v_A, v_B, v_C, $\cdots$ and entropies S_A, S_B, S_C, $\cdots$, the whole system at a common temperature T. Assume for simplicity that external work changes in the system only involve mechanical energy. For any infinitesimal change occurring in the system, for example, to the component A, it follows, from the first law, that

$$dq_A = dE_A + p_A dv_A. \tag{24.1}$$

It may here be observed, for re-emphasis, that whereas dE has the properties of a complete differential, the same is not true of dq (Section 4.). The corre-

sponding entropy change will be

$$dS_A = \frac{dq_A}{T} = \frac{dE_A + p_A dv_A}{T}.$$ (24.2)

Similar equations hold for other changes in the system. Since the system is assumed isolated,

$$dq_A + dq_B + dq_C + \cdots = 0.$$

Hence

$$dS_A + dS_B + dS_C + \cdots = \frac{dq_A + dq_B + dq_C + \cdots}{T} = 0.$$ (24.3)

Or alternatively,

$$d(S_A + S_B + S_C + \cdots) = 0.$$ (24.4)

In other words, the entropy of an isolated system remains unchanged. Consequently, the change of entropy in an adiabatic process is zero. Also, the entropy of the system is equal to the sum of the entropies of the component parts of the system.

(25) **Entropy Change in an Ideal Gas:** For an ideal gas the heat absorbed in any process of change

$$q = \Delta E + p\Delta v.$$ (25.1)

For an infinitesimal change,

$$dq = dE + pdv.$$

Hence

$$dS = \frac{dq}{T} = \frac{dE + pdv}{T} = \frac{C_v dT + pdv}{T}.$$ (25.2)

If C_v is independent of temperature,

$$S = \int dS = C_v \int \frac{dT}{T} + R \int \frac{dv}{v} + \text{constant}$$ (25.3)

$$= C_v \ln T + R \ln v + \text{constant}.$$ (25.4)

For a definite volume change, for example, an isothermal compression from v_A to v_B of one mole of gas,

$$S_B - S_A = R \ln \frac{v_B}{v_A}.$$ (25.5)

Since v_B is less than v_A, it is evident that the entropy of an ideal gas decreases during an isothermal compression. Conversely, in an isothermal expansion, the entropy of the gas increases by an amount equal to $R \ln (v_B/v_A)$, where v_B is now greater than v_A.

If equation (25.4) be expressed in the form

$$S = C_v \ln T + R \ln v + S_0,$$ (25.6)

where S_0 is the integration constant, the following transformation is possible

in the case of an ideal gas. The volume v may be replaced by RT/p and, since $C_p - C_v = R$ (14.6), there results

$$S = C_p \ln T - R \ln p + S_0',$$ (25.7)

where $S_0' = S_0 + R \ln R$.

Applying this expression to a mixture of ideal gases at partial pressures $p_1, p_2, \cdots$, it follows that the entropy of a mole of the gases in the mixture is given by equations of the form

$$S_1 = C_{p,1} \ln T - R \ln p_1 + S'_{0,1},$$ (25.8)

$$S_2 = C_{p,2} \ln T - R \ln p_2 + S'_{0,2}.$$ (25.9)

For a mixture of n_1 moles at pressure p_1 with n_2 moles at pressure p_2,

$$S = n_1(C_{p,1} \ln T - R \ln p_1 + S'_{0,1}) + n_2(C_{p,2} \ln T - R \ln p_2 + S'_{0,2}).$$ (25.10)

If p is the total pressure, then, by Dalton's Law, $p_1 = x_1 p$ and $p_2 = x_2 p$ where x_1 and x_2 are the respective mole fractions. Hence,

$$S = n_1(C_{p,1} \ln T - R \ln p - R \ln x_1 + S'_{0,1})$$
$$+ n_2(C_{p,2} \ln T - R \ln p - R \ln x_2 + S'_{0,2}).$$ (25.11)

If the entropy of the mixture at the total pressure p be compared with the sum of the entropies of the pure gases each at pressure p, it is obvious that the entropy of mixing of ideal gases at constant pressure is

$$\Delta S = -n_1 R \ln x_1 - n_2 R \ln x_2.$$ (25.12)

Since x_1 and x_2 are fractions, it follows that the entropy change on mixing is a positive quantity.

(26) **Entropy Change with Volume and Pressure:** Equation (25.2) may be written in the form,

$$T dS = dE + p dv.$$ (26.1)

For an isothermal process it follows that

$$p = T \left(\frac{\partial S}{\partial v} \right)_T - \left(\frac{\partial E}{\partial v} \right)_T.$$ (26.2)

This expression may be differentiated with respect to temperature, the volume being assumed constant,

$$\left(\frac{\partial p}{\partial T} \right)_v = T \frac{\partial^2 S}{\partial T \partial v} + \left(\frac{\partial S}{\partial v} \right)_T - \frac{\partial^2 E}{\partial T \partial v}.$$ (26.3)

Now since, at constant volume,

$$dS = C_v \frac{dT}{T},$$ (26.4)

it follows that

$$\left(\frac{\partial S}{\partial T}\right)_v = \frac{C_v}{T} \quad \text{and} \quad \frac{\partial^2 S}{\partial v \partial T} = \frac{1}{T}\left(\frac{\partial C_v}{\partial v}\right)_T. \tag{26.5}$$

Also

$$\frac{1}{T}\left(\frac{\partial^2 E}{\partial T \partial v}\right) = \frac{1}{T}\left(\frac{\partial C_v}{dv}\right)_T, \tag{26.6}$$

since

$$\left(\frac{\partial E}{\partial T}\right)_v = C_v. \tag{6.3}$$

Hence, from equations (26.3), (26.5) and (26.6)

$$\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial S}{\partial v}\right)_T, \tag{26.7}$$

which is the desired variation of entropy with volume.

Similarly, with respect to the variation of entropy with pressure, since

$$H = E + pv, \qquad dH = dE + pdv + vdp = TdS + vdp. \tag{26.8}$$

Hence,

$$v = -T\left(\frac{\partial S}{\partial p}\right)_T + \left(\frac{\partial H}{\partial p}\right)_T. \tag{26.9}$$

By differentiating further with respect to temperature and again eliminating identities we obtain

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p. \tag{26.10}$$

It will be noted that these are general expressions applicable alike to all states of matter and, indeed, to equilibria involving one or more phases of matter.

(27) **Entropy Change with Temperature:** From equation (26.5) of the preceding section the change of entropy with temperature at constant volume is equal to C_v/T. Correspondingly, at constant pressure, the entropy change with temperature is given by the expression

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}. \tag{27.1}$$

It follows, therefore, that the entropy change over a finite temperature range from T_1 to T_2 at constant pressure is

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T}\, dT = \int_{T_1}^{T_2} C_p d \ln T. \tag{27.2}$$

To evaluate such an integral it is therefore necessary to know the variation of heat capacity with temperature. This known, the integral may be solved

either graphically or with some empirical or theoretical expression for the heat capacity as a function of the temperature. (See Chapter IV.)

(28) Entropy Change in Irreversible Processes: The transfer of heat from a hotter to a colder system constitutes a simple irreversible process. Let us imagine an isolated system consisting of two reservoirs at temperatures T_2 and T_1 ($T_2 > T_1$) and a machine, e.g., an ideal gas, by which heat may be transferred. By allowing the gas to expand isothermally in the reservoir of heat at T_2, an amount of heat q may be taken from the reservoir. The gas may now be allowed to expand adiabatically until a temperature T_1 is attained. By placing the gas in contact with reservoir at T_1 and isothermally compressing, an amount of heat, q, may be communicated to the reservoir at T_1. The change in entropy of the gas is

$$\frac{q}{T_2} - \frac{q}{T_1} . \tag{28.1}$$

The change in entropy of the reservoirs considered as a system is equal to

$$- \frac{q}{T_2} + \frac{q}{T_1} = \frac{q}{T_1} - \frac{q}{T_2} . \tag{28.2}$$

Now, since T_2 is greater than T_1, we conclude that the conduction of heat from a reservoir of high temperature to one of low temperature results in an increase of entropy of the reservoir system.

The expansion of an ideal gas from volume v_A to volume v_B against a vacuum is another irreversible process, in which, as already shown,

$$S_B - S_A = R \ln \frac{v_B}{v_A} , \tag{28.3}$$

in which therefore an entropy increase of the gaseous system results.

More generally, as indicated in Section 23, the efficiency of an irreversible cycle is less than that of a reversible cycle, or $(\sum q/T)_{\text{irr.}} < 0$. For a given system, say an ideal gas, undergoing a cycle ABA, composed of an irreversible path, A to B, followed by a reversible path, B to A, it follows that

$$\int_A^B \frac{\mathrm{d}q'}{T} + \int_B^A \frac{\mathrm{d}q}{T} < 0, \tag{28.4}$$

where the prime superscript indicates irreversible elements in the path. The expression may be rewritten in the form

$$\int_A^B \frac{\mathrm{d}q'}{T} + S_A - S_B < 0 \tag{28.5}$$

or

$$\int_A^B \frac{\mathrm{d}q'}{T} < S_B - S_A. \tag{28.6}$$

The integral quantity in the irreversible stage is less than the increase in entropy of the system as it changes from State A to State B. The heat reservoir from which the system withdrew the heat has suffered a change in entropy of $\int_A^B \dfrac{dq'}{T}$, since the heat may be assumed to have been removed reversibly. Hence, in the irreversible path, A to B, the entropy of the system plus reservoir has increased. In the reversible path B to A there is no net change in the entropy of the system plus reservoir. The whole cycle however is an irreversible cycle since it is irreversible in part. It is accompanied by an increase of entropy of the whole, system plus reservoirs.

These conclusions with regard to entropy change may be generalized in the following manner. In irreversible processes, the entropy of all the systems involved in the change is increased. In ideal reversible processes, the entropy of the system as a whole is unchanged. The change in entropy of any portion of such a system undergoing a reversible change is equal to the heat which such portion of the system absorbs divided by the absolute temperature at which the heat is absorbed.

Now since all real processes are irreversible, one method of statement of the Second Law of Thermodynamics follows. *All naturally occurring processes are accompanied by an increase in the entropy of the system.* The content of the two laws of thermodynamics may therefore be summed up in the aphorism of Clausius: "The energy of the universe is constant; the entropy of the universe tends towards a maximum." This formulation of the second law provides us with one criterion of the direction of change which a given system will take if allowed to change spontaneously. The change will occur in that direction in which an increase in the entropy of the system is obtained.

(29) **Free Energy:** The concept of entropy gained applicability to problems of chemical change in its most useful form after the theorem of Nernst, sometimes termed the Third Law of Thermodynamics, was formulated in 1906. Upon the basis of the Nernst Theorem (see Chapter IV) it became possible to determine molal entropies of reactant materials at any temperature and thus to determine the direction of chemical change. Prior to this development the concepts embodied in the second law were formulated on the one hand in terms of "free energy" as developed by Helmholtz and on the other in terms of "thermodynamic potential" by Gibbs, which function subsequently was termed free energy by Lewis and Randall in their systematization of modern thermodynamics applied to chemistry.

These two thermodynamic functions may be defined in the following manner. The Helmholtz free energy, A, is defined by the expression,

$$A = E - TS, \tag{29.1}$$

and the Gibbs (Lewis) free energy function is defined by the equation,

$$F = H - TS. \tag{29.2}$$

The two free energies bear, therefore, the same relation to one another that the internal energy, E, bears to the heat content, H,

$$F = H - TS = (E + pv) - TS = A + pv. \tag{29.3}$$

For an isothermal change, these several thermodynamic functions may be related in the expressions,

$$\Delta A = \Delta E - T\Delta S \tag{29.4}$$

and

$$\Delta F = \Delta H - T\Delta S, \qquad \cdot \tag{29.5}$$

from which, at constant pressure, the relation follows,

$$\Delta F = \Delta A + p\Delta v. \tag{29.6}$$

For a reversible change at constant temperature T, the quantity $T\Delta S$ is equal to the heat, q, absorbed in the process. Also, from the application of the first law to such a reversible isothermal process,

$$\Delta E = q - W_r, \tag{29.7}$$

whence, it is seen that

$$\Delta A = (- W_r)_T, \tag{29.8}$$

which associates the change in Helmholtz free energy with the maximum work available in an isothermal reversible process. Lewis and Randall refer to the quantity A, therefore, as the maximum work function.

In a process at constant temperature and constant pressure it is obvious that the work w done by the system will be composite of two factors, that involved in the volume change, $p\Delta v$, and a residual quantity, w', which may be one of many energy quantities. A frequent form of energy obtained in the conduct of chemical processes is electrical energy. Radiant energy, in the form of light, may be produced. The quantity $p\Delta v$ is constant irrespective of the mode of conduct of the process. The magnitude of the quantity w', on the other hand, will vary with the mode of conduct of the process. Thus, silver and iodine may be caused to react spontaneously to form silver iodide, for example, in a calorimeter at atmospheric pressure with the performance of no other external work than that·involved in the $p\Delta v$ term. In this case the reaction results in the evolution of 15 kcal. of heat per mole of silver iodide formed. On the other hand, the same reaction can be effected in a galvanic cell, in which case there is a net absorption of heat equivalent to 0.75 kcal. since, in addition to the $p\Delta v$ term, the external work performed by the system included electrical energy equal to 15.75 kcal. per mole of silver iodide formed.

The greater the degree of irreversibility there is in the mode of conduct of the process, the smaller will w' be. The more the process approximates to reversible conditions the greater will w' be, and, in the limit, with a completely reversible process, it will become equal to its maximum value, W_r'. Hence,

for a completely reversible isothermal process at constant pressure,

$$W_r = p\Delta v + W_r' = -\Delta A. \tag{29.9}$$

Since from equation (29.6), $\Delta F = \Delta A + p\Delta v$, it follows immediately that

$$W_r' = -\Delta F. \tag{29.10}$$

The decrease in Gibbs free energy, ΔF, is therefore equal to the net work done by the system, operating reversibly, exclusive of the work $p\Delta v$ done against the external pressure. It is this free energy which is normally the preferred free energy function since most chemical experiments are carried out under constant pressure conditions. For reactions at constant volume and constant pressure it is obvious that $\Delta A = \Delta F$.

(30) **The Relations between Free Energy and Entropy:** Differentiation of the equation (29.1) for the Helmholtz free energy, $A = E - TS$, yields

$$dA = dE - TdS - SdT. \tag{30.1}$$

Applying the equation of the first law, $dq = dE + pdv$, and restricting the external work to the mechanical work due to the volume change, it follows that

$$dA = dq - pdv - TdS - SdT. \tag{30.2}$$

If dq is supplied reversibly, it is equal to TdS and hence,

$$dA = -pdv - SdT. \tag{30.3}$$

Therefore, for a reversible change at constant volume, $(dv = 0)$,

$$\left(\frac{\partial A}{\partial T}\right)_v = -S. \tag{30.4}$$

Further, at constant temperature, $dA = -pdv$, or, for an ideal gas in which $pv = RT$, for a volume change, v_1 to v_2,

$$\Delta A = -\int_{v_1}^{v_2} pdv$$

$$= RT \ln \frac{v_1}{v_2}. \tag{30.5}$$

Similarly, for the Gibbs free energy function, $F = H - TS$, since $H = E + pv$, differentiation yields

$$dF = dE + pdv + vdp - TdS - SdT. \tag{30.6}$$

For a reversible change, with the same simplifications,

$$dF = vdp - SdT, \tag{30.7}$$

and, hence, at constant pressure

$$\left(\frac{\partial F}{\partial T}\right)_p = -S. \tag{30.8}$$

These equations are applicable to physical changes occurring in the system, exclusive of chemical reaction, the amounts of the constituents of the system present being assumed unaltered in the changes occurring.

(31) **Free Energy Change with Pressure**: Differentiation of the Gibbs free energy function $F = H - TS$ with respect to pressure at constant temperature gives

$$\left(\frac{\partial F}{\partial p}\right)_T = \left(\frac{\partial H}{\partial p}\right)_T - T\left(\frac{\partial S}{\partial p}\right)_T. \tag{31.1}$$

Since $H = E + pv$,

$$dH = dE + pdv + vdp$$
$$= TdS + vdp.$$

Hence,

$$v = \left(\frac{\partial H}{\partial p}\right)_T - T\left(\frac{\partial S}{\partial p}\right)_T \tag{31.2}$$

and, consequently

$$\left(\frac{\partial F}{\partial p}\right)_T = v. \tag{31.3}$$

For an isothermal process it follows that,

$$\int dF = \int vdp \tag{31.4}$$

or, for a finite pressure change from p_1 to p_2 with an ideal gas,

$$\Delta F = \int_{p_1}^{p_2} vdp = RT \ln \frac{p_2}{p_1}. \tag{31.5}$$

(32) **Free Energy Change with Temperature**: Differentiation of the Gibbs free energy function with respect to temperature at constant pressure yields

$$\left(\frac{\partial F}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p - T\left(\frac{\partial S}{\partial T}\right)_p - S. \tag{32.1}$$

It has already been shown that both $(\partial H/\partial T)_p$ and $T(\partial S/\partial T)_p$ are equal to C_p, hence

$$\left(\frac{\partial F}{\partial T}\right)_p = -S = \frac{F - H}{T}, \tag{32.2}$$

$$F - H = T\left(\frac{\partial F}{\partial T}\right)_p. \tag{32.3}$$

(33) **The Gibbs-Helmholtz Equation:** Equation (30.7) for a system at constant pressure may be written in the form,

$$dF = -SdT. \tag{33.1}$$

For a reversible change, from state A to state B, at constant pressure, it follows that

$$dF_A = -S_A dT \qquad \text{and} \qquad dF_B = -S_B dT. \tag{33.2}$$

By subtraction

$$d(F_B - F_A) = -(S_B - S_A)dT \tag{33.3}$$

or

$$d(\Delta F) = -\Delta S dT. \tag{33.4}$$

At constant pressure, therefore,

$$\left(\frac{\partial (\Delta F)}{\partial T} \right)_p = -\Delta S. \tag{33.5}$$

If this value for ΔS is introduced into equation (29.5) it follows that

$$\Delta F - \Delta H = T \left(\frac{\partial \Delta F}{\partial T} \right)_p. \tag{33.6}$$

A corresponding derivation, employing the Helmholtz free energy in the form

$$dA = -SdT, \tag{33.7}$$

yields the analogous expression, applicable to an isothermal reversible change at constant volume,

$$\Delta A - \Delta E = T \left(\frac{\partial \Delta A}{\partial T} \right)_v. \tag{33.8}$$

These two alternative forms of the Gibbs-Helmholtz equation relate the change in internal energy ΔE and the change in heat content ΔH to the corresponding changes in free energy and their temperature coefficients. Applied to reversible galvanic cells they permit the determination of the change in heat content accompanying the cell reaction from measurements of the electromotive force E and the temperature coefficient of electromotive force dE/dT. At constant pressure

$$-\Delta F = n\text{FE}, \tag{33.9}$$

where $n\text{F}$ is the number of coulombs of electricity yielded by the cell reaction, F is a faraday of electricity, and the cell is operated under such circumstances as will yield the maximum electrical work. The Gibbs-Helmholtz equation assumes the form

$$-n\text{FE} - \Delta H = -n\text{F}T \left(\frac{\partial \text{E}}{\partial T} \right)_p \tag{33.10}$$

or

$$n\mathrm{FE} + \Delta H = n\mathrm{F}T \left(\frac{\partial \mathrm{E}}{\partial T} \right)_p. \qquad (33.11)$$

(34) Thermodynamic Equilibrium: A condition of equilibrium may be defined by stating that a system is in equilibrium when it shows no change of state in any particular with time. The system must be in a state of absolute rest. A state of partial equilibrium is familiar to every one. A mixture of hydrogen and oxygen at room temperatures is one such example already discussed in an earlier section.

A state of absolute rest is difficult to determine experimentally. This fact may be illustrated by the case of the mixture of hydrogen and oxygen just cited. If, for example, such a gas mixture were stored over mercury at room temperature, no change in volume would be noted over long periods of time. This does not mean, however, that no chemical change is occurring. Let it be assumed that 10^6 molecules of hydrogen and half this number of oxygen molecules are reacting *per second*. A simple calculation, employing for the Avogadro number, $N = 6.03 \times 10^{23}$ molecules per gram molecule, will reveal that it would require a period of observation extending over 2×10^6 years before a volume contraction of 1 cc. could be observed. It is very evident, therefore, that any thermodynamic criteria for a state of absolute rest or of chemical equilibrium would be extremely valuable if not absolutely necessary.

The thermodynamic functions of entropy and free energy may be utilized to provide such criteria of equilibrium. It has already been indicated that the conduct of a reversible process actually produces a succession of equilibrium states each differing infinitesimally from the next. In an isolated system, as already shown (Section 24), the entropy remains unchanged, that is,

$$dS = 0, \qquad (24.4)$$

which therefore becomes a criterion of equilibrium in such a system. Since in an isolated system q and w are zero it follows that ΔE is also zero, and so the criterion of reversibility may be stated in the form,

$$(\partial S)_{E,v} = 0. \qquad (34.1)$$

This criterion applies also to equilibrium in an adiabatic system. For a reversible process, also, in which there is no exchange of energy with the surroundings other than that involved in the volume change,

$$dF = -SdT + vdp, \qquad (30.7)$$

whence, for such reversible changes at constant pressure and temperature,

$$dF = 0 \qquad (34.2)$$

or

$$(\partial F)_{p,T} = 0.$$

Similarly, for the Helmholtz free energy change dA, which from equation (30.3) is equal to $- pdv - SdT$, it follows that

$$(\partial A)_{v,T} = 0 \qquad (34.4)$$

is a characteristic of small reversible changes occurring in a system at equilibrium.

A system which is not in equilibrium tends to proceed spontaneously towards the state of equilibrium. Spontaneously occurring processes are accompanied by an increase in the entropy of the system. A maximum value for the entropy of the system is reached when the system attains equilibrium. When this condition is reached $dS = 0$. From the thermodynamic expression, applicable to systems at constant pressure and temperature,

$$\Delta F = \Delta H - T\Delta S, \qquad (29.5)$$

since ΔH is constant at constant temperature and characteristic of the process of change, the increase of entropy of a spontaneous process at constant temperature and pressure is accompanied by a decrease in free energy to a minimum value when equilibrium is attained. When this condition is reached $(\partial F)_{p,T} = 0$.

Such a condition of equilibrium may be more readily understood by consideration of an equilibrium process, e.g., white and gray tin at the transition temperature, 18° C. and 1 atm., in a galvanic cell. Under such circumstances, the electromotive force of the cell is zero, and no transformation occurs. When an external electromotive force dE is imposed on the cell disturbing the equilibrium obtaining in the cell system, the free energy change is expressed by the equation

$$dF = - n\mathrm{F}dE. \qquad (34.5)$$

As before, $n\mathrm{F}$ is the number of coulombs of electricity involved, F being the faraday. The smaller the value of dE the smaller is the free energy change, dF and the smaller the disturbance of the equilibrium. As dE approaches zero so does dF approach zero. If the reaction occurring could be performed exactly at equilibrium ($dE = 0$), then the change of free energy would be zero.

Even for processes involving change of temperature and pressure at equilibrium the free energy change is zero. For example, consider an equilibrium between two states of matter, a liquid in equilibrium with its saturated vapor. The expression

$$dF = vdp - SdT \qquad (30.7)$$

may be employed. If equilibrium can obtain at temperature T and pressure p and also at $T + dT$ and $p + dp$ respectively, an infinitesimal displacement of the system from its equilibrium by changing pressure alone at constant temperature T or of temperature alone at constant pressure p involves the two free energy changes

$$dF = vdp \qquad \text{and} \qquad dF = - SdT, \qquad (34.6)$$

A simultaneous change of p and T by the amounts dp and dT necessary to the establishment of a new state of equilibrium satisfies the condition

$$dF = vdp - SdT = 0.$$

It is evident that one could thus proceed by a series of infinitesimal steps from a given position of equilibrium in a liquid-vapor system at pressure p_1 and temperature T_1 to a new position of equilibrium at pressure p_2 and temperature T_2, each step in the process involving zero free energy change and, hence, for the overall process, $\Delta F = 0$.

Quite generally, therefore, for all processes occurring at equilibrium,

$$\Delta F_{eq.} = 0. \tag{34.7}$$

(35) **The Clapeyron-Clausius Equation:** The variation in pressure with temperature in an equilibrium between two states of matter may be deduced, with the aid of the free energy relation, $dF = 0$, just obtained and from equation (26.7) for entropy change with volume. Applying this latter expression

$$\left(\frac{\partial p}{\partial T} \right)_v = \left(\frac{\partial S}{\partial v} \right)_p \tag{26.7}$$

to the process of vaporization, it is to be noted that the pressure p is independent of the volume. Furthermore, the infinitesimal dS/dv may be replaced by the expression $\Delta S/\Delta v$ which refers to one mole of the substance in question. Hence, for the vaporization of any substance,

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta v}. \tag{35.1}$$

For any system in equilibrium, since $\Delta F_{eq.} = 0$,

$$\Delta S = \frac{\Delta H}{T}. \tag{35.2}$$

Equation (35.1) therefore becomes

$$\frac{dp}{dT} = \frac{\Delta H}{T \Delta v}. \tag{35.3}$$

In this equation ΔH is actually the latent heat of vaporization λ of the substance so that

$$\frac{dp}{dT} = \frac{\lambda}{T \Delta v}. \tag{35.4}$$

This expression, which is quite generally applicable, can be transformed into a familiar form when applied to vapors sufficiently dilute that the equation $pv = RT$ can be assumed to hold and the volume of the vapor is large com-

pared with that of the condensed system. In such case, the equation becomes

$$\frac{dp}{dT} = \frac{\lambda}{T(v_g - v_l)} \tag{35.5}$$

or, neglecting v_l,

$$\frac{dp}{dT} = \frac{\lambda}{T \cdot \dfrac{RT}{p}} \tag{35.6}$$

or

$$\frac{dp/p}{dT} = \frac{\lambda}{RT^2} \tag{35.7}$$

or

$$\frac{d \ln p}{dT} = \frac{\lambda}{RT^2} \tag{35.8}$$

(36) **Entropy Change Accompanying Fusion and Vaporization:** At the freezing point and boiling point, these processes of fusion and vaporization are respectively equilibrium processes. With pure substances the temperature is constant. In each case therefore

$$T\Delta S = \Delta H, \tag{36.1}$$

where ΔH is the latent heat of fusion or vaporization and T is the absolute temperature of the fusion or vaporization.

The same equation is applicable also to a transition from one crystalline form of matter to another where T is the transition temperature and ΔH is the heat of transition.

PARTIAL MOLAL QUANTITIES

(37) **General Considerations:** The value of a thermodynamic function, for example, the internal energy, of a simple substance of one component in a given state in reference to some standard state is determined by the variables of condition, the pressure, the volume and the temperature. Thus,

$$E = f(p, v, T) + E^0, \tag{37.1}$$

where E^0 is the internal energy in a normal state, arbitrarily selected. There is always some relation, such as

$$f(p, v, T) = 0, \tag{37.2}$$

which is called an equation of state of the substance, and as a result of which one of the variables depends on the other two. It is then possible to evaluate the function by means of any two independent variables. Thus,

$$E = f(v, T) + E^0 = f(p, T) + E^0, \text{ etc.,} \tag{37.3}$$

is true for any simple substance.

A thermodynamic function of a phase composed of two or more components is not determined by two of the above independent variables, but is only determined by two of these variables and the masses of the components. We shall find it most convenient to choose the pressure and temperature as well as the masses as the independent variables. The internal energy of a given phase may be expressed by

$$E = f(p, T, m_1, m_2, \ldots, m_c) + E^0. \tag{37.4}$$

In like manner the general equation for the free energy of the phase is

$$F = f'(p, T, m_1, m_2, \ldots, m_c) + F^0, \tag{37.5}$$

where m_1, m_2, etc., are the masses of the c components of the phase, and F^0 is the free energy of an arbitrarily selected state. If we now consider an infinitesimal change in F and partially differentiate the right-hand member of this equation, we obtain

$$dF = \frac{\partial F}{\partial p} dp + \frac{\partial F}{\partial T} dT + \frac{\partial F}{\partial m_1} dm_1 + \frac{\partial F}{\partial m_2} dm_2 + \ldots + \frac{\partial F}{\partial m_c} dm_c. \tag{37.6}$$

But, according to equation (30.7),

$$\partial F = -SdT + vdp$$

for a phase, or a system of phases at constant composition, and, therefore,

$$dF = -SdT + vdp + \frac{\partial F}{\partial m_1} dm_1 + \frac{\partial F}{\partial m_2} dm_2 + \ldots + \frac{\partial F}{\partial m_c} dm_c. \tag{37.8}$$

In general, we shall make these partial derivatives in respect to mass equal to μ_1, μ_2, etc., respectively, according to the notation of Gibbs, and, as a consequence, equation (37.8) becomes

$$dF = -SdT + vdp + \mu_1 dm_1 + \mu_2 dm_2 + \ldots + \mu_c dm_c \tag{37.9}$$

and, at constant pressure and temperature,

$$dF = \mu_1 \partial m_1 + \mu_2 \partial m_2 + \ldots + \mu_c \partial m_c. \tag{37.10}$$

Equation (37.9), which was originally obtained by Gibbs, and relations immediately deducible from it, may serve as a general fundamental relation underlying the thermodynamics of solutions. This equation is valid for any phase of a c component system. By considering a system of p phases, and by using an equation similar to this but involving the energy, Gibbs [1] in his famous memoir was able to deduce the phase rule. It should always be borne in mind that·

---

[1] Transactions of the Connecticut Academy (1875–1878). Scientific Papers of Willard Gibbs, Vol. 1. Longmans and Co.

equation (37.9) and similar ones make possible an exact study of systems of many components in one phase, or many phases. In considering complicated chemical systems, there is no safer method than to employ these general equations of Gibbs.[1] An important conclusion for the discussion in hand is the principle, immediately deducible upon application of equation (37.9) to a system of phases, that when a polycomponent system in p phases is in stable equilibrium, and, if μ_1, μ_1', ..., μ_1^p represent the μ values of the first component, μ_2, μ_2', ..., μ_2^p represent the μ values of the second component throughout the p phases, etc., for the c components, then, at constant pressure and temperature,

$$\left.\begin{array}{l} \mu_1 = \mu_1' = \mu_1'' \ldots = \mu_1^p, \\ \mu_2 = \mu_2' = \mu_2'' \ldots = \mu_2^p, \text{ etc.} \end{array}\right\} \quad (37.11)$$

It was because of this property of these partial derivatives that Gibbs denoted them the "chemical potentials."

Like the entropy or internal energy, the free energy of a homogeneous system is doubled if its mass is doubled. From this property, and from inspection of equation (37.9), it is clear that μ_1, μ_2, etc., are independent of the masses, and depend only on the composition, or relative quantities of the components, and the units in which the free energy and masses are expressed. As a consequence, equations (37.9) or (37.10) may be integrated term by term. Equation (37.10) thus becomes

$$F = \mu_1 m_1 + \mu_2 m_2 + \ldots + \mu_c m_c. \quad (37.12)$$

Complete differentiation of this latter equation gives

$$dF = \mu_1 \partial m_1 + m_1 \partial \mu_1 + \mu_2 \partial m_2 + m_2 \partial \mu_2 + \ldots + \mu_c \partial m_c + m_c \partial \mu_c. \quad (37.13)$$

Elimination of dF from (37.10) and (37.13) gives the important equation

$$m_1 \partial \mu_1 + m_2 \partial \mu_2 + \ldots + m_c \partial \mu_c = 0. \quad (37.14)$$

We have yet to consider the units in which these quantities may be expressed, and, for the sake of simplicity, let us choose a phase of two components. If (37.12) is divided by $m_1 + m_2$ or the total mass, we obtain

$$\frac{F}{m_1 + m_2} = \left(\frac{m_1}{m_1 + m_2}\right)\mu_1 + \left(\frac{m_2}{m_1 + m_2}\right)\mu_2. \quad (37.15)$$

Thus, if $F/(m_1 + m_2)$ is the free energy per gram, $m_1/(m_1 + m_2)$ and $m_2/(m_1 + m_2)$ are the weight fractions of the components, and μ_1, μ_2 or $\partial F/\partial m_1$, $\partial F/\partial m_2$ may be denoted partial specific free energies. In a similar manner, the free energy per mole of a phase may be defined by $F/(n_1 + n_2)$, where n_1 and n_2 are the number of moles of each component, respectively. Substituting moles

[1] Williamson and Morey, *J. Am. Chem. Soc.*, **40**, 49 (1917); Morey and Williamson, *ibid.*, **40**, 59 (1917); Morey, *J. Franklin Inst.*, **194**, 425 (1922).

for grams, we obtain according to (37.12)

$$\frac{F}{n_1 + n_2} = \frac{n_1}{n_1 + n_2}\bar{F}_1 + \frac{n_2}{n_1 + n_2}\bar{F}_2,$$

where μ_1 and μ_2 are now $\bar{F}_1$ and $\bar{F}_2$, the partial molal free energies, and n_1' $(n_1 + n_2)$ and $n_2/(n_1 + n_2)$, which we denote x_1 and x_2, are the mole fractions.

Thus, denoting the free energy per mole, F, we may write (37.12) and (37.14)

$$F = x_1\bar{F}_1 + x_2\bar{F}_2 + \ldots + x_c\bar{F}_c \tag{37.16}$$

and

$$0 = x_1\partial\bar{F}_1 + x_2\partial\bar{F}_2 + \ldots + x_c\partial\bar{F}_c. \tag{37.17}$$

Now, in the same manner, it is possible to regard many quantities such as the heat content, the volume, the entropy, the heat capacity, etc., as functions of the masses only when the pressure and temperature of the system are constant, and, consequently, the same general method of partial differentiation may be applied. In general, if we let G equal the value of the property of 1 mole of the whole phase, we have the following three fundamental and useful equations of partial molal quantities, namely,

$$dG = \bar{G}_1\partial x_1 + \bar{G}_2\partial x_2 + \ldots + \bar{G}_c\partial x_c, \tag{37.18}$$

$$G = \bar{G}_1 x_1 + \bar{G}_2 x_2 + \ldots + \bar{G}_c x_c, \tag{37.19}$$

$$0 = x_1\partial\bar{G}_1 + x_2\partial\bar{G}_2 + \ldots + x_c\partial\bar{G}_c. \tag{37.20}$$

By the use of the general thermodynamic equations of Gibbs and the consideration of units, we are thus brought into contact with a class of quantities which are of utmost importance in the thermodynamics of solutions. The development of this subject since the time of Gibbs, and, particularly, the methods of employing the partial molal quantities in numerical calculations have been brought about very largely by the researches of Lewis and his colleagues.[1]

(38) **The Direct Determination of Partial Molal Heat Content from Calorimetric Data:** The physical significance of partial quantities may be clearly understood by considering the heat of dilution by water of a salt solution of a given concentration. For this purpose, the data of Stearn and Smith[2] may be employed on the heat of dilution of a 2.9 molal strontium chloride solution by different quantities of water. The results given in Table IV are for experiments at 25° and 1 atmosphere. If the heat of dilution is positive, the system evolves heat as a result of the change, and, consequently, there will be a decrease in heat content or vice versa.

---

[1] These investigations have been revised and corrected and a very comprehensive treatment of the subject has been presented by Lewis and Randall, Thermodynamics. McGraw-Hill Book Co. (1923).

[2] *J. Am. Chem. Soc.*, **42**, 18 (1920).

TABLE IV

HEAT CONTENT DECREASE, AND MOLAL HEAT CONTENT DECREASE OF 2.9 M STRONTIUM
CHLORIDE ON DILUTION BY DIFFERENT QUANTITIES OF WATER

Δn_1 Water of Dilution (Moles)	$- \Delta H$ Total Heat of Dilution (Cal.)	$- \Delta H / \Delta n_1$ Mean Heat Content Decrease per Mole (Cal.)
37.2	129.8	3.49
30.0	112.4	3.75
30.0	114.1	3.80
27.7	109.2	3.95
20.0	86.3	4.31
19.5	85.4	4.38
10.0	48.5	4.85

In Fig. 4, the values of $- \Delta H / \Delta n_1$ are plotted against the number of moles of water added. This plot is a straight line and, consequently, the results may be extrapolated to zero Δn_1. It is thus found that $- \Delta H / \Delta n_1$ equals 5.4 when Δn_1 equals zero. This is exactly the definition of the derivative of $- H$ with respect to n_1, and, since it refers to the heat content change produced by one of the components while the mass of the other component is constant, it equals the negative of $\partial H / \partial n_1$, or $\bar{H}_1$, the partial molal heat content of the component water. Or, we may equally well say that $\bar{H}_1$ equals the change of heat content of an infinitely large quantity of the solution on the addition of a mole of water.

FIG. 4. Molal Heat Content Decrease of Strontium Chloride

(39) **Relative Partial Molal Heat Contents:** By a series of measurements of the kind just illustrated, Stearn and Smith obtained the partial molal heat content of water in strontium chloride solutions of different concentrations. In tabulating a partial molal quantity, it is necessary to refer its value to another standard state. It is convenient to employ as a standard state an infinitely dilute solution. Thus, for a change in a partial molal quantity of the water or strontium chloride in the above solution, we would have $(\bar{G}_1 - \bar{G}_1^0)$ and $(\bar{G}_2 - \bar{G}_2^0)$, respectively. In all the subsequent discussion the subscript 1 will refer to the water, and the subscript 2 to the solute. The partial molal quantity of the solvent in pure solvent, or $\bar{G}_1^0$, is zero and, consequently, this case is

very simple. Following throughout the notation of Lewis and Randall, we shall let these differences of partial heat contents equal $\bar{L}_1$, $\bar{L}_2$, respectively, and call these quantities the relative partial molal heat contents. In Table V, the data of Stearn and Smith on the relative partial heat contents of water at different molal concentrations of strontium chloride are given.

TABLE V

RELATIVE PARTIAL MOLAL HEAT CONTENTS OF WATER IN STRONTIUM
CHLORIDE SOLUTIONS AT 25°

c	L_1
0	0.00
0.20	−0.25
0.425	−0.50
0.80	−0.62
1.20	−0.90
1.55	−1.11
2.00	−1.75
2.4	−2.10
2.9	−5.40
3.2	−7.20

(40) **Partial Molal Heat Capacity:** The heat capacity, C_p, of a solution at constant pressure containing n_1 moles of solvent and n_2 moles of solute is equal to $(\partial H/\partial T)_p$ where H is the heat content of the solution. If this expression is differentiated with respect to n_1 when n_2 is maintained constant,

$$\frac{\partial^2 H}{\partial T \partial n_1} = \left(\frac{\partial C_p}{\partial n_1}\right)_{n_2} = \bar{C}_{p,1}, \tag{40.1}$$

where $\bar{C}_{p,1}$ is the partial molal heat capacity of the solvent. Since

$$\left(\frac{\partial H}{\partial n_1}\right)_{n_2} = \bar{H}_1,$$

it follows by differentiation that

$$\frac{\partial^2 H}{\partial T \partial n_1} = \frac{\partial \bar{H}_1}{\partial T} = \bar{C}_{p,1}. \tag{40.2}$$

Also, since $\bar{L}_1 = \bar{H}_1 - \bar{H}_1^0$, it follows that

$$\frac{\partial \bar{L}_1}{\partial T} = \frac{\partial \bar{H}_1}{\partial T} - \frac{\partial \bar{H}_1^0}{\partial T} = \bar{C}_{p,1} - \bar{C}_{p,1}^0 \tag{40.3}$$

It is apparent that $\bar{C}_{p,1}^0$ is actually the molal heat capacity of the pure solvent. Similarly,

$$\frac{\partial \bar{L}_2}{\partial T} = \frac{\partial \bar{H}_2}{\partial T} - \frac{\partial \bar{H}_2^0}{\partial T} = \bar{C}_{p,2} - \bar{C}_{p,2}^0, \tag{40.4}$$

where $\bar{C}_{p,2}$ and $\bar{C}_{p,2}^0$ are the partial molal heat capacities of the solute in the

given solution and at infinite dilution. The difference between the two quantities is the relative partial molal heat capacity of the substance.

(41) Partial Molal Free Energy and Heat Content from Electromotive Force Measurements: Measurements of the electromotive forces of cells of the type

$$Ag \,|\, AgCl \,|\, HCl(m_2) \,|\, Pt, \; H_2 \,|\, HCl(m_1) \,|\, AgCl \,|\, Ag$$
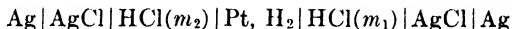
and of the temperature coefficients of such electromotive forces can be used with the aid of the Gibbs-Helmholtz equation to determine the changes in the free energy and the heat content of the cell reaction. This reaction is obviously a concentration change

$$HCl(m_2) \;=\; HCl(m_1).$$

The net effect of the cell reaction is the reversible transfer of a mole of hydrochloric acid from a solution of molal concentration, m_2, to a solution of molal concentration, m_1. The electromotive force is a measure of a free energy change, $\Delta \bar{F}$, which may be regarded as composite of two quantities, $\bar{F}_{2,2}$ and $\bar{F}_{2,1}$, the former the change in free energy when one mole of hydrochloric acid as solute is added to an infinitely large quantity of solution of concentration, m_2, and $\bar{F}_{2,1}$ the corresponding change for one mole of hydrochloric acid added to an infinitely large quantity of solution of concentration, m_1. These two quantities $\bar{F}_{2,2}$ and $\bar{F}_{2,1}$ denote the partial molal free energies of the hydrochloric acid in the two solutions, the partial molal free energy being the greater in the more concentrated solution. If $m_2 > m_1$, then since $\Delta \bar{F} = \bar{F}_{2,2} - \bar{F}_{2,1}$, there will be a decrease in free energy, as expected, in a transfer from a more concentrated to a more dilute solution.

Similarly from the electromotive force and its temperature coefficient, the change in heat content accompanying the dilution process may be determined. The change in heat content, $\Delta \bar{H}$, is again composite of two quantities $\bar{H}_{2,1}$ and $\bar{H}_{2,2}$ the partial molal heat contents of the solute in the two solutions of concentrations m_1 and m_2. It is also obvious that these several quantities could have been obtained by combining measurements on two cell combinations, e.g.,

$$H_2, \; Pt \,|\, HCl(m_2) \,|\, AgCl \,|\, Ag$$
$$H_2, \; Pt \,|\, HCl(m_1) \,|\, AgCl \,|\, Ag.$$
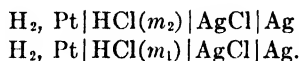
As illustrative of such data, Table VI presents the changes in heat content and in free energy in joules at 25° C. when one mole of hydrochloric acid is transferred from a solution of concentration m to a solution of 0.1 molal concentration.

(42) Calculation of Relative Partial Molal Heat Content of Solvent from that of the Solute: Applying equation (37.19) to the heat content, the following equations result,

$$H = x_1 \bar{H}_1 + x_2 \bar{H}_2 \tag{42.1}$$

and

$$H^0 = x_1 \bar{H}_1^0 + x_2 \bar{H}_2^0. \tag{42.2}$$

TABLE VI

CHANGES IN HEAT CONTENT AND FREE ENERGY IN JOULES WHEN 1 MOLE OF HYDROCHLORIC
ACID IS TRANSFERRED FROM CONCENTRATION m TO 0.1 M. AT 25° C.

m	$-\Delta H$	$-\Delta \bar{F}$
4.484	8474	23544
1.928	3591	15744
1.038	1937	11679
0.771	1619	9971
0.509	999	7757
0.338	260	5856
0.1	0	0
0.0332	− 435	− 5138
0.00948	− 745	−11044
0.00338	− 915	−15898
0.000999	− 930	−21878
0	−1050 (extrapolated)	− ∞

From these it follows that, L, the total relative heat content, $H - H^0$ is

$$L = x_1 \bar{L}_1 + x_2 \bar{L}_2. \qquad (42.3)$$

Also, from equation (37.20),

$$0 = x_1 \partial \bar{L}_1 + x_2 \partial \bar{L}_2, \qquad (42.4)$$

from which it is possible to determine the value of the relative partial molal heat content of the solvent when that of the solute is known, or vice versa. Thus,

$$\bar{L}_1 = - \int \frac{x_2}{x_1} d\bar{L}_2, \qquad (42.5)$$

for the evaluation of which integral graphical methods can be employed. Figure 5 shows a plot of x_2/x_1 against $\bar{L}_2$ for hydrochloric acid. The value of
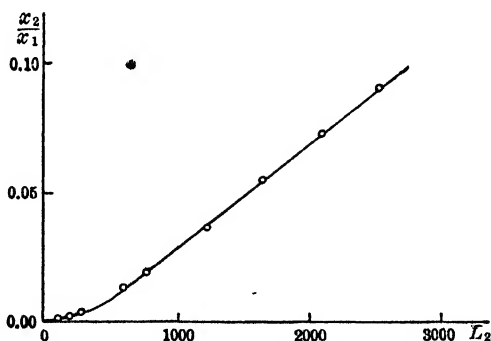
FIG. 5.   Relative Partial Molal Heat Content of Hydrochloric Acid

the integral is given by the area under the curve from 0 to a given value of x_2/x_1. Typical results so obtained for hydrochloric acid and sodium chloride solutions are given in Table VII.

TABLE VII

RELATIVE PARTIAL MOLAL HEAT CONTENTS (IN CALORIES) OF HYDROCHLORIC ACID AND
WATER IN HYDROCHLORIC ACID SOLUTIONS AND SODIUM CHLORIDE
AND WATER IN SODIUM CHLORIDE SOLUTIONS

m	$\dfrac{r_2}{r_1}$	HCl		NaCl	
		L_1	L_2	$\bar{L}_1$	$\bar{L}_2$
0	0	0	0	0	0
0.001	0.000018	—	25.1	—	—
0.01	0.00018	− 0.012	78.9	0.01	− 1
0.05	0.0009	− 0.052	177	0.03	− 3
0.1	0.0018	− 0.161	251	0.05	− 8
0.5	0.009	− 1.16	496	0.65	−120
1	0.018	− 3.66	747	3.4	−332
2	0.036	− 15.8	1206	10.0	−564
3	0.054	− 37.7	1651	17.4	−736
4	0.072	− 66.6	2103	21.9	−810
5	0.09	−103.6	2541	19.4	−779

(43) **Partial Molal Free Energy and Solute Concentration:** From equation (31.3), at constant temperature, $dF = vdp$, it follows that, for an ideal gas, in which RT/p can be substituted for v,

$$\int dF = RT \int \frac{dp}{p} \tag{43.1}$$

or

$$F = RT \ln p + \text{constant.} \tag{43.2}$$

A similar procedure is applicable also to ideal solutions in which the osmotic pressure of the solute can be substituted for the gas pressure. Moreover, since the osmotic pressure is proportional to the concentration in ideal solutions, we may express the fundamental equation for the relative partial molal free energy of an ideal solute at concentration m in solution at high dilution at constant temperature by the equation,

$$\bar{F} - \bar{F}^0 = RT \ln m + I, \tag{43.3}$$

where the constant I is a function of an arbitrarily defined standard state $\bar{F}^0$. Applied to electrolytes as solutes in extremely dilute solutions the expression takes the form,

$$\bar{F} - \bar{F}^0 = \nu RT \ln m + I, \tag{43.4}$$

where ν is the number of ions which one molecule of the electrolyte yields on solution. Such equations for electrolytes are actually strictly valid only at infinite dilution. In two papers,[1] G. N. Lewis introduced two new functions,

[1] G. N. Lewis, *Proc. Am. Acad.*, **37**, 45 (1901); **43**, 259 (1907).

the fugacity and the activity, into thermodynamic chemistry. The latter function has been largely employed, since 1912, in studies of the thermodynamic properties of solutions of electrolytes and ions in solution.

<div align="center">THE ACTIVITY FUNCTION</div>

(44) **Definition of Activity:** The activity of a component of a system may be defined by the equation

$$F = RT \ln \xi + i, \tag{44.1}$$

where ξ is the activity in general and i is a constant.

The absolute value of the free energy being indeterminate, the free energy is measured in reference to some standard state F^0. Hence,

$$F - F^0 = RT \ln \frac{\xi}{\xi^0} = RT \ln a, \tag{44.2}$$

where ξ^0 is the activity when $F - F^0$ is zero. Under these circumstances ξ/ξ^0 is the relative activity, a, now generally termed the activity, which is the form of the activity function commonly employed.

Also, the relative activity of a molecular or ionic species in a phase of variable composition will be related to the partial free energy by the equation,

$$\bar{F} - \bar{F}^0 = RT \ln a. \tag{44.3}$$

In this equation the relationship of the activity to the molar concentration of a solute in an ideal solution as expressed in (43.3) is apparent.

(45) **Activity and Equilibrium in a Chemical Reaction:** Consider a generalized reaction at constant temperature and pressure in which n_1 moles of A_1, etc., n_2 moles of A_2, etc., and n_3 moles of A_3, etc., react to form n_1' moles of A_1', etc., n_2' moles of A_2', etc., and n_3' moles of A_3', etc., where the moles with the subscript 1 refer to gases, 2 to solutions, and 3 to liquids and solids. Thus

$$n_1 A_1 + \cdots n_2 A_2 + \cdots n_3 A_3 + \cdots = n_1' A_1' + \cdots n_2' A_2' + \cdots n_3' A_3' + \cdots.$$
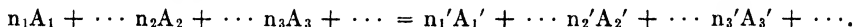
According to equations (44.2) and (44.3),

$$(F - F^0)_{A_1} = n_1 RT \ln a_{A_1}, \text{ etc.,}$$
$$(\bar{F} - \bar{F}^0)_{A_2} = n_1 RT \ln a_{A_2}, \text{ etc.,}$$

and

$$(F - F^0)_{A_1'} = n_1' RT \ln a_{A_1'}, \text{ etc.,}$$
$$(\bar{F} - \bar{F}^0)_{A_2'} = n_2' RT \ln a_{A_2'}, \text{ etc.}$$

The total change in free energy of the reaction will be

$$[(F - F^0)_{A_1'} + (\bar{F} - \bar{F}^0)_{A_2'} + \cdots] - [(F - F^0)_{A_1} + (\bar{F} - \bar{F}^0)_{A_2} + \cdots]$$
$$= RT \ln \frac{a_{A_1'}^{n_1'} \cdots a_{A_2'}^{n_2'} \cdots a_{A_3'}^{n_3'} \cdots}{a_{A_1}^{n_1} \cdots a_{A_2}^{n_2} \cdots a_{A_3}^{n_3} \cdots}. \tag{45.1}$$

If we let

$$\Delta F = (F_{A_1'} + \bar{F}_{A_2'} + \cdots) - (F_{A_1} + \bar{F}_{A_2} + \cdots)$$

and

$$\Delta F^0 = (F^0_{A_1'} + \bar{F}^0_{A_2'} + \cdots) - (F^0_{A_1} + \bar{F}^0_{A_2} + \cdots),$$

we obtain

$$\Delta F - \Delta F^0 = RT \ln \frac{a_{A_1'}^{n_1'} \cdots a_{A_2'}^{n_2'} \cdots a_{A_3'}^{n_3'} \cdots}{a_{A_1}^{n_1} \cdots a_{A_2}^{n_2} \cdots a_{A_3}^{n_3} \cdots} . \tag{45.2}$$

ΔF is the free energy change of the reaction in general, and $(\Delta F - \Delta F^0)$ is the free energy change of the reaction in reference to the standard state.

When the reaction is in equilibrium at constant temperature and pressure, the condition that $\Delta F = 0$ must be fulfilled, and, consequently,

$$\Delta F^0 = - RT \ln \frac{a_{A_1'}^{n_1'} \cdots a_{A_2'}^{n_2'} \cdots a_{A_3'}^{n_3'} \cdots}{a_{A_1}^{n_1} \cdots a_{A_2}^{n_2} \cdots a_{A_3}^{n_3} \cdots} . \tag{45.3}$$

Since ΔF^0 is a constant, we have at constant temperature and pressure

$$K = \frac{a_{A_1'}^{n_1'} \cdots a_{A_2'}^{n_2'} \cdots a_{A_3'}^{n_3'} \cdots}{a_{A_1}^{n_1} \cdots a_{A_2}^{n_2} \cdots a_{A_3}^{n_3} \cdots} , \tag{45.4}$$

where K is the equilibrium constant of the reaction. This general equation, which is entirely similar in form to the mass action law, has the advantage of being exact.

(46) **Activity and Temperature:** The Gibbs-Helmholtz equation (32.3) may be employed in the form

$$\frac{\partial \left(\dfrac{F}{T} \right)}{\partial T} = - \frac{H}{T^2}, \tag{46.1}$$

where F and H are to be referred to arbitrary standard states. Further, according to equation (37.16), the free energy of a phase of c components is expressed by

$$F = x_1 \bar{F}_1 + x_2 \bar{F}_2 + \cdots + x_c \bar{F}_c, \tag{37.16}$$

or if each of these quantities be referred to arbitrary standard states,

$$F - F^0 = x_1(\bar{F}_1 - \bar{F}_1^0) + x_2(\bar{F}_2 - \bar{F}_2^0) + \cdots + x_c(\bar{F}_c - \bar{F}_c^0) \tag{46.2}$$

is obtained. We may now introduce the activities by equation (44.3) and obtain

$$F - F^0 = x_1 RT \ln a_1 + x_2 RT \ln a_2 + \cdots + x_c RT \ln a_c. \tag{46.3}$$

Similarly, according to the general equation for partial quantities and equation (42.3), the total heat content will be

$$H - H^0 = x_1 \bar{L}_1 + x_2 \bar{L}_2 + \cdots + x_c \bar{L}_c. \tag{46.4}$$

Substituting these values of $(F - F^0)$ and $(H - H^0)$ for F and H in equation (46.1), and performing the differentiation at constant composition, we obtain

$$\left[\frac{x_1 \partial \ln a_1 + x_2 \partial \ln a_2 + \cdots + x_c \partial \ln a_c}{dT} \right]_{p,x}$$
$$= \frac{-(x_1 \bar{L}_1 + x_2 \bar{L}_2 + \cdots + x_c \bar{L}_c)}{RT^2} . \quad (46.5)$$

This is the general equation for the variation of the activities of the components of a mixture with the temperature at constant composition.

Let us consider the case where "1 mole of solution," which consists of x_1 moles of the first component, x_2 moles of the second component, etc., is transferred from a solution of one composition to that of another composition. In this case, the partial free energy and heat content increments will be

$$F'' - F' = x_1(\bar{F}_1'' - \bar{F}_1') + x_2(\bar{F}_2'' - \bar{F}_2') + \cdots + x_c(\bar{F}_c'' - \bar{F}_c') \quad (46.6)$$

$$= x_1 RT \ln \frac{a_1''}{a_1'} + x_2 RT \ln \frac{a_2''}{a_2'} + \cdots + x_c RT \ln \frac{a_c''}{a_c'} \quad (46.7)$$

and

$$H'' - H' = x_1(\bar{L}_1'' - \bar{L}_1') + x_2(\bar{L}_2'' - \bar{L}_2') + \cdots + x_c(\bar{L}_c'' - \bar{L}_c'). \quad (46.8)$$

Substituting these values for ΔF and ΔH in equation (46.1), and performing the differentiation at constant composition, we obtain

$$\left[\frac{x_1 \partial \ln \frac{a_1''}{a_2'} + x_2 \partial \ln \frac{a_2''}{a_2'} + \cdots + x_c \partial \ln \frac{a_c''}{a_c'}}{\partial T} \right]_{p,x}$$
$$= - \frac{[x_1(\bar{L}_1'' - \bar{L}_1') + x_2(\bar{L}_2'' - \bar{L}_2') + \cdots + x_c(\bar{L}_c'' - \bar{L}_c')]}{RT^2} . \quad (46.9)$$

Usually, the transfer of 1 mole of a single component is considered. In this case, it is obvious that

$$\frac{\partial \left(\ln \frac{a''}{a'} \right)}{\partial T} = - \frac{(\bar{L}'' - \bar{L}')}{RT^2} . \quad (46.10)$$

Although many symbols are required to perform these deductions accurately, the principles involved are quite simple. If 1 mole of a component is transferred, then ΔF is the partial free energy change and ΔH is the relative partial heat content change of the transfer. If 1 mole of solution is transferred, then ΔF is the mole fraction times the partial free energy change of the first component plus the mole fraction times the partial free energy change of the

second component, etc., and ΔH is the mole fraction times the relative partial heat content change of the first component plus, etc.

In order to integrate equation (46.10), or others like it, it is necessary to know $\bar{L}'' - \bar{L}'$ as a function of the temperature. Such a relation is given by equation (9.3), from which it is clear that

$$\frac{\partial(\bar{L}'' - \bar{L}')}{\partial T} = \bar{C}_p'' - \bar{C}_p', \qquad (46.11)$$

where $\bar{C}_p''$ and $\bar{C}_p'$ are the partial molal specific heats at constant pressure at the two concentrations, respectively.

(47) **Activity and Pressure:** From the differential of the free energy at constant composition, $\partial F = -S\partial T + v\partial p$, by differentiation with respect to p, at constant temperature, we obtain

$$\left[\frac{\partial F}{\partial p}\right]_T = v. \qquad (47.1)$$

According to the general equation (37.19) for partial quantities, the total volume V will be given by

$$V = x_1\bar{V}_1 + x_2\bar{V}_2 + \cdots + x_c\bar{V}_c, \qquad (47.2)$$

where $\bar{V}_1$, $\bar{V}_2$, etc., are the partial volumes. Substituting for F the value given by (46.3), and for V the value given by (47.2), we obtain

$$\left[\frac{x_1\partial \ln a_1 + x_2\partial \ln a_2 + \cdots + x_c\partial \ln a_c}{\partial p}\right]_{T,x}$$
$$= \frac{x_1\bar{V}_1 + x_2\bar{V}_2 + \cdots + x_c\bar{V}_c}{RT} \qquad (47.3)$$

and for a single component

$$\left[\frac{\partial \ln a}{\partial p}\right]_{T,x} = \frac{\bar{V}_1}{RT}. \qquad (47.4)$$

Thermodynamics and Statistics

(48) **The Statistical Nature of the Second Law:** The second law of thermodynamics applies only to macroscopic systems, those containing large numbers of molecules. The laws relating to the pressure exerted by a gas and the work which it may perform or to the position of equilibrium in a given system are not applicable to systems containing but few molecules. With the aid of suitable thermodynamic data the physical chemist can foretell what will happen when a few cubic centimeters of hydrogen chloride and of ammonia are admixed under stated conditions of temperature and pressure but his laws are unable to predict the behavior of a few molecules of each. The position of equilibrium becomes definite when the number of molecules is so large that a substantial

uniformity of distribution occurs. Such an assemblage of molecules cannot be equally spaced in the containing vessel nor, due to impacts, will their velocities be uniform. The direction of change which a system in such a hypothetical state of equal spacing and uniform velocity would spontaneously suffer would be towards a greater state of randomness of distribution, to a system of greater disorder in space and velocity. Such a spontaneous change always results, as we have seen, in an increase in the entropy of the system. For this reason Boltzmann (1896) associated the entropy of the system with its thermodynamic probability, W, this being defined as the ratio of the probability of an actual state to one of the same volume and total energy having a completely ordered arrangement of its molecular constituents. The relation may be generally formulated by the expression $S = f(W)$. Now since, in the case of two systems, the entropy of the combined system S is obtained by adding the individual entropies, S_1 and S_2, whereas the probabilities must be multiplied, $W = W_1 \times W_2$, it is evident that the functional relation between the two must be logarithmic and we may write

$$S = k \ln W + \text{constant.} \qquad (48.1)$$

Boltzmann found that the constant k was equal to the gas constant per molecule ($= R/N$), where N is Avogadro's number. If the entropy depends only on the thermodynamic probability, then the constant is zero and $S = k \ln W$. This condition was envisaged by Planck, with the result that, at the absolute zero of temperature, where a completely ordered molecular arrangement might in favorable circumstances be expected to hold, the probability W would be unity and the entropy corresponding would be zero. It will be shown in Chap. IV that this is one formulation of the Heat Theorem of Nernst, sometimes called the Third Law of Thermodynamics.

The definition of the entropy of a system and the associated thermodynamic quantities in terms of the thermodynamic probability may be expected therefore to result from the development of our knowledge of the statistical distributions which occur in such large numbers of molecules as are dealt with in the ordinary processes of chemical change. It is to this problem, the central problem of statistical mechanics, that we may now turn.[1]

(49) **The Boltzmann Distribution Law:** The fundamental equation of statistical mechanics is the Boltzmann law of energy distribution. To derive this law we consider a system of s distinguishable harmonic oscillators in equilibrium with a system A (not necessarily another oscillator but which may be such). The harmonic oscillator can take up energy in integral multiples of $h\nu$, where ν is the fundamental frequency of the oscillator and h is Planck's constant.

The problem to be solved is the determination of the probability $P(\epsilon)$ that the system A shall have an amount of energy ϵ if the total amount of energy available is E.

---

[1] In the succeeding sections we follow a mode of presentation developed by H. Eyring and J. Walter, *J. Chem. Ed.*, **18**, 73 (1941).

The following assumptions are made:

(1) Any particular way of distributing the energy $E - \epsilon$ among the oscillators is equally probable.

(2) The number of different ways in which the energy $E - \epsilon$ can be distributed among the distinguishable oscillators is proportional to the probability that the system A has an energy ϵ in a particular state.

In Fig. 6, each of the dots represents a different way of distributing the energy $E - \epsilon$ or less among two oscillators. If $E - \epsilon$ is large, the number of different ways N_2 of distributing the energy $E - \epsilon$ or less is given by the area of the triangle two of whose sides have lengths $E - \epsilon$ in units of $h\nu$. That is, $N_2 = (E - \epsilon)^2/2!$

Similarly, for the case of 3 oscillators, the number of different ways, N_3, of distributing the energy $E - \epsilon$ or less is given by the volume of a pyramid having three rectangular axes of length $E - \epsilon$ as edges. That is, $N_3 = (E - \epsilon)^3/3!$

For s oscillators, in the same way, the number of ways N_s of distributing the energy $E - \epsilon$ or less will be, $N_s = (E - \epsilon)^s/s!$ Also, the

Fig 6

number of ways in which the energy $E - \epsilon$ can be distributed will be given by the surface area of the s-dimensional volume. Hence, using assumption (2),

$$P(\epsilon) = a' \frac{dN_s}{d\epsilon} \cong (E - \epsilon)^{s-1} \cong E^{s-1}(1 - \epsilon/E)^{s-1} = a(1 - \epsilon/E)^{s-1}, \quad (49.1)$$

where a' is a proportionality constant. Since ϵ is negligible in comparison with the total energy E, we may write $E = s\bar{E}$ where $\bar{E}$ is the average energy. With this substitution, and using the binomial theorem,

$$P(\epsilon) = a(1 - \epsilon/s\bar{E})^{s-1}$$
$$= a\left[1 - \frac{s-1}{s} \cdot \frac{\epsilon}{\bar{E}} + \frac{(s-1)(s-2)}{s^2 \cdot 2!}\left(\frac{\epsilon}{\bar{E}} \right)^2 \right.$$
$$\left. - \frac{(s-1)(s-2)(s-3)}{s^3 \cdot 3!}\left(\frac{\epsilon}{\bar{E}} \right)^3 + \cdots \right]. \quad (49.2)$$

If s is a large number, the expression becomes, to a very close approximation,

$$P(\epsilon) = a\left(1 - \frac{\epsilon}{\bar{E}} + \frac{1}{2!}\left(\frac{\epsilon}{\bar{E}} \right)^2 - \frac{1}{3!}\left(\frac{\epsilon}{\bar{E}} \right)^3 + \cdots \right)$$
$$= ae^{-\epsilon/\bar{E}}. \quad (49.3)$$
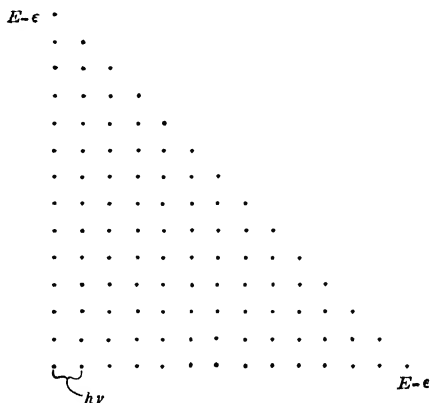
This is the required probability. The value of the constant a is readily determined. Let ϵ_n denote a particular value of ϵ. Since the probability that A be in some state is unity, it follows that

$$\sum_n P(\epsilon_n) = a \sum_n e^{-\epsilon_n/\bar{E}} = 1. \tag{49.4}$$

Hence,

$$a = 1/(\sum_n e^{-\epsilon_n/\bar{E}}), \tag{49.5}$$

and

$$P(\epsilon) = e^{-\epsilon/\bar{E}}/\sum_n e^{-\epsilon_n/E}. \tag{49.6}$$

Case 1: The system A is a harmonic oscillator. In such case, $\epsilon_n = nh\nu$. The probability becomes therefore

$$P(nh\nu) = e^{-nh\nu/E}/\sum_n e^{-nh\nu/\bar{E}}. \tag{49.7}$$

A crystal composed of N atoms may be considered as a set of $3N$ harmonic oscillators. At high temperatures the heat capacity of such a crystal, by the familiar law of Dulong and Petit, is $3R$ calories per mole which is equivalent to k calories per oscillator where k is the Boltzmann constant. The average value $\bar{E}$ of the energy in the equations given may be evaluated by calculating the high temperature heat capacity of an oscillator. The total energy E is given by the sum of the products of the energy of each state and the probability that the oscillator be in that state

$$E = \sum_n P(nh\nu)nh\nu = \frac{\sum_n nh\nu e^{-nh\nu/E}}{\sum_n e^{-nh\nu/E}}, \tag{49.8}$$

which transforms readily to

$$E = -\frac{d}{d(1/\bar{E})} \ln (\sum_n e^{-nh\nu/\bar{E}}). \tag{49.9}$$

Now,

$$\sum_n e^{-nh\nu/\bar{E}} = 1 + e^{-h\nu/\bar{E}} + e^{-2h\nu/\bar{E}} + \cdots$$
$$= (1 - e^{-h\nu/\bar{E}})^{-1}. \tag{49.10}$$

Hence,

$$E = -\frac{d}{d(1/\bar{E})} \ln (1 - e^{-h\nu/\bar{E}})^{-1}$$

$$= \frac{h\nu}{e^{h\nu/E} - 1} = \frac{h\nu}{\dfrac{h\nu}{\bar{E}} + \dfrac{1}{2!}\left(\dfrac{h\nu}{\bar{E}}\right)^2 + \dfrac{1}{3!}\left(\dfrac{h\nu}{\bar{E}}\right)^3 + \cdots}. \tag{49.11}$$

If $\bar{E} \gg h\nu$, which is true at high temperatures, the expression neglecting higher powers of $(h\nu/\bar{E})$ becomes,

$$E = h\nu/(h\nu/\bar{E}) = \bar{E}. \tag{49.12}$$

Since, also, the heat capacity is equal to dE/dT it follows for an oscillator that

$$dE/dT = d\bar{E}/dT = k, \tag{49.13}$$

and, by integration, $\bar{E} = kT + c$ where c is a constant. Since, at $T° \text{ K.} = 0$, the energy is zero, we see from the expression $E = h\nu/(e^{h\nu/(kT+c)} - 1)$ that the constant c must be zero. Hence, since the average energy $\bar{E}$ has the value kT, the fundamental equation for the probability $P(\epsilon_i)$ that any molecular system have the energy ϵ_i in a single state, becomes

$$P(\epsilon_i) = \frac{e^{-\epsilon_i/kT}}{\sum_i e^{-\epsilon_i/kT}}. \tag{49.14}$$

If the energy ϵ_i can be taken up in more than one way, the probability of having the energy ϵ_i will be increased by a factor g_i, the "statistical weight" which is the number of ways in which the energy ϵ_i can be absorbed. Then,

$$P(\epsilon_i) = \frac{g_i e^{-\epsilon_i/kT}}{\sum_i g_i e^{-\epsilon_i/kT}}. \tag{49.15}$$

Case 2: Suppose a system has s modes of taking up energy according to the law

$$E = cn^r, \tag{49.16}$$

where c is a constant and n is an integer, then the number of ways in which the system can have energy $E - \epsilon$ or less is given by

$$N = a(E - \epsilon)^{s/r}. \tag{49.17}$$

The number of ways in which the system can have the actual energy $E - \epsilon$ is

$$P(E - \epsilon) = \frac{dN}{dE} = b\left(1 - \frac{\epsilon}{E}\right)^{\frac{s}{r} - 1} \tag{49.18}$$

Suppose the energy considered is translational and that the system has N_0 non-interacting (distinguishable) molecules; each molecule has 3 modes of taking up energy so that the total number of modes is $3N_0$, and, since this is equivalent to s, it follows that

$$P(E - \epsilon) = b\left(1 - \frac{\epsilon}{E}\right)^{\frac{3N_0}{r} - 1} \tag{49.19}$$

To the system of N_0 molecules, possessing translational energy only, is now added another molecule; suppose the total energy is now E. The probability $P(\epsilon)$ that the added molecule shall have the precise amount of energy ϵ of any one kind, translational, vibrational, rotational, etc., is simply equal to the

probability that the remaining N_0 molecules shall have the energy $E - \epsilon$ in the $3N_0$ translational modes.   The required probability is, therefore, the value given by equation (49.19), or,

$$P(\epsilon) = b \left(1 - \frac{\epsilon}{E} \right)^{\frac{3N_0}{r} - 1} \tag{49.20}$$

Again expanding by the binomial theorem, assuming also that ϵ/E is small while N_0 is large, the result is

$$\begin{aligned} P(\epsilon) &= ae^{-3N_0\epsilon/rE} \\ &= ae^{-\epsilon/\beta}, \end{aligned} \tag{49.21}$$

where $\beta = rE/3N_0$.   The energy ϵ may be any kind of energy as noted above.   The magnitude of the constant a can be evaluated as in (49.5) to give $a = 1/\sum_n e^{-\epsilon/\beta}$.   The value of β can be shown to be equal to kT by the familiar application of the distribution equation (see Vol. II) to the determination of the pressure of a gas, considering the quantity ϵ as a component of velocity in a given direction, equal to $\frac{1}{2} mu^2$, and comparing the result with the equation of state for a gas $pv = NkT$.

Alternatively, accepting the conclusion from quantum mechanics for a particle in a box, that translational energy is taken up according to the law $E = cn^2$, then $r = 2$ and β may be calculated as follows.   Consider ϵ as translational energy: the chance that ϵ shall be in the group of translational states with quantum numbers lying between n_x and $n_x + dn_x$, n_y and $n_y + dn_y$ and n_z and $n_z + dn_z$ is,

$$P = ae^{-\epsilon/\beta} dn_x dn_y dn_z. \tag{49.22}$$

Using the relations, $\epsilon_x = c_x n_x^2 = \frac{1}{2}mv_x^2$, and similar expressions for ϵ_y and ϵ_z, the probability that a molecule shall have components of velocity between v_x and $v_x + dv_x$, v_y and $v_y + dv_y$ and v_z and $v_z + dv_z$ is

$$P = be^{-mv^2/2\beta} v^2 dv, \tag{49.23}$$

where $v^2 = v_x^2 + v_y^2 + v_z^2$.   The fraction of molecules with velocities between v and $v + dv$ is therefore,

$$\frac{dN}{N} = \frac{e^{-mv^2/2\beta} v^2 dv}{\int_0^\infty e^{-mv^2/2\beta} v^2 dv} = 4\pi \left(\frac{m}{2\pi\beta} \right)^{3/2} e^{-mv^2/2\beta} v^2 dv. \tag{49.24}$$

The mean square velocity $\bar{v}^2$ is given by,

$$\begin{aligned} \bar{v}^2 &= \int_0^\infty v^2 \frac{dN}{N} = 4\pi \left(\frac{m}{2\pi\beta} \right)^{3/2} \int_0^\infty e^{-mv^2/2\beta} v^4 dv \\ &= \frac{3\beta}{m} . \end{aligned} \tag{49.25}$$

From kinetic theory, for an ideal gas,

$$\tfrac{1}{3}Nm\bar{v}^2 = RT. \tag{49.26}$$

Hence,

$$v^2 = \frac{3RT}{Nm} = \frac{3kT}{m}, \tag{49.27}$$

whence, from (49.25) and (49.27)

$$\beta = kT. \tag{49.28}$$

Hence, it follows that,

(i) the probability that a molecule shall have precisely the energy ϵ_i *of any kind*, i.e., in any quantum state, is

$$P(\epsilon_i) = \frac{e^{-\epsilon_i/kT}}{\sum\limits_i e^{-\epsilon_i/kT}} \tag{49.29}$$

with the corresponding modification, cf. equation (49.15), in case a 'statistical weight' factor, g_i, is operative.

(ii) Maxwell's Law of Distribution of Velocities is given

$$\frac{dN}{N} = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-mv^2/2kT} v^2 dv. \tag{49.30}$$

(50) **The Partition Function:** The summation term $\sum\limits_i e^{-\epsilon_i/kT}$ which enters into the denominator of the expression for $P(\epsilon_i)$ constitutes an important quantity which may be related to the various thermodynamic quantities already obtained. For obvious reasons it has been called the state-sum or sum of the states (zustandssumme) and also the distribution function, but recently, the term partition function has been most frequently employed for the expression. We may assign it the symbol f and define it explicitly:

$$f = \sum_i e^{-\epsilon_i/kT} = e^{-\epsilon_0/kT} + e^{-\epsilon_1/kT} + e^{-\epsilon_2/kT} + \cdots + e^{-\epsilon_i/kT}, \tag{50.1}$$

where the summation extends over all the possible energy states of the system, each term multiplied where necessary by its statistical weight g_i when the given energy state can be achieved in more than one way.

(51) **Internal Energy and the Partition Function:** The internal energy of a molecular system in excess of that at the absolute zero is given by the expression

$$E - E_0 = N_0\epsilon_0 + N_1\epsilon_1 + N_2\epsilon_2 + \cdots + N_i\epsilon_i, \tag{51.1}$$

where $N_0, N_1, N_2, \cdots, N_i$ are the numbers of molecules in the system possessing respectively the energies $\epsilon_0, \epsilon_1, \epsilon_2, \cdots, \epsilon_i$. Since quite generally

$$N_i = N(P(\epsilon_i)) = Ne^{-\epsilon_i/kT}/f,$$

$$E - E_0 = \frac{N}{f}e^{-\epsilon_0/kT}\epsilon_0 + \frac{N}{f}e^{-\epsilon_1/kT}\epsilon_1 + \frac{N}{f}e^{-\epsilon_2/kT}\epsilon_2 + \cdots + \frac{N}{f}e^{-\epsilon_i/kT}\epsilon_i. \tag{51.2}$$

Differentiating f with respect to temperature gives

$$\frac{df}{dT} = e^{-\epsilon_0/kT} \cdot \frac{\epsilon_0}{kT^2} + e^{-\epsilon_1/kT} \cdot \frac{\epsilon_1}{kT^2} + \cdots + e^{-\epsilon_i/kT} \cdot \frac{\epsilon_i}{kT^2} \cdot \qquad (51.3)$$

Hence, for 1 mole, where N is the Avogadro number,

$$E - E_0 = \frac{N}{f} kT^2 \frac{df}{dT} = NkT^2 \frac{d \ln f}{dT} \cdot \qquad (51.4)$$

(52) Heat Capacity and the Partition Function: The internal energy per mole of a system is expressible in the form

$$E = E_0 + NkT^2 \frac{d \ln f}{dT} \cdot \qquad (52.1)$$

Now, since $(\partial E/\partial T)_v = C_v$, it follows that

$$C_v = \frac{\partial}{\partial T} \left(NkT^2 \frac{\partial \ln f}{\partial T} \right)_v \qquad (52.2)$$

expresses the heat capacity in terms of the partition function. The expression is restricted to constant volume because, as will later be shown, the partition function for translational energy is dependent on the volume of the system.

(53) Equilibrium and the Partition Function: In an equilibrium existing between two molecular species, $A \rightleftarrows B$, the probability that the system will be in the state B_i with energy ϵ_{B_i} is given by the expression $P(\epsilon_{B_i}) = ae^{-\epsilon_{B_i}/kT}$. Similarly the probability that it will be in the state A_i with energy ϵ_{A_i} is $ae^{-\epsilon_{A_i}/kT}$. The state of equilibrium is determined by the ratio of the probability that the system be in any of the states corresponding to B to the probability that the system be in any of the states corresponding to A, since this ratio is that of the number of molecules B to the number of molecules A in the given volume, v. This ratio which is the equilibrium constant is therefore

$$K_c = \frac{a \sum_i e^{-\epsilon_{B_i}/kT}/v}{a \sum_i e^{-\epsilon_{A_i}/kT}/v} = \frac{f_B}{f_A} \cdot \qquad (53.1)$$

(54) Standard Free Energy Change and the Partition Function: In any ideal gas reaction, generalized by the equation,

$$aA + bB = cC + dD,$$
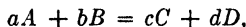
the relation between the standard free energy change and the equilibrium constant in terms of concentrations is representable by the expression

$$\Delta F^0 = -RT \ln K_c \qquad (54.1)$$

or

$$\Delta F^0 = cF_C^0 + dF_D^0 - aF_A^0 - bF_B^0 = -RT \ln \frac{C_C{}^c C_D{}^d}{C_A{}^a C_B{}^b}, \qquad (54.2)$$

where C_A, C_B, C_C, and C_D refer to the equilibrium concentrations. From the relation of the preceding section it follows therefore that

$$cF_C^0 + dF_D^0 - aF_A^0 - bF_B^0$$

$$= -RT \left\{ \ln \left(\frac{f_C}{v} \right)^c + \ln \left(\frac{f_D}{v} \right)^d - \ln \left(\frac{f_A}{v} \right)^a - \ln \left(\frac{f_B}{v} \right)^b \right\} . \quad (54.3)$$

By identifying terms on each side of the expression it is evident that a series of relations are obtained of the type

$$cF_C^0 = -RT \ln \left(\frac{f_C}{v} \right)^c + \text{const.,} \quad (54.4)$$

the constant, in each case, being a function of the particular species only, which must cancel each other in the case of a system in equilibrium and which may, for simplicity, be set equal to zero. There results, accordingly, the general expression

$$F^0 = -RT \ln \frac{f}{v} . \quad (54.5)$$

Since the free energy per mole is given by the expression

$$F = F^0 + RT \ln \frac{N}{v} , \quad (54.6)$$

it follows that

$$F = -RT \ln \frac{f}{v} + RT \ln \frac{N}{v} \quad (54.7)$$

$$= -RT \ln \frac{f}{N} = -kT \ln \left(\frac{f}{N} \right)^N \quad (54.8)$$

$$= -NkT \ln \left(\frac{f}{N} \right)^* : \quad (54.9)$$

* A more general method of deriving expressions for the Gibbs and Helmholtz free energies in terms of the partition function, which, however, involves the conclusion of the Third Law of Thermodynamics, that $S_0 = 0$ (see Chapter IV), is given in the following manner. The average value of the internal energy, $\bar{E}$, is given by the expression,

$$\bar{E} = \frac{\sum_i E_i e^{-E_i/kT}}{\sum_i e^{-E_i/kT}} = kT^2 \left(\frac{\partial}{\partial T} \ln \sum_i e^{-E_i/kT} \right)_v . \quad (54.10)$$

Hence,

$$C_v = \left(\frac{\partial \bar{E}}{\partial T} \right)_v = \frac{\partial}{\partial T} \left[kT^2 \left(\frac{\partial}{\partial T} \ln \sum_i e^{-E_i/kT} \right)_v \right] \quad (54.11)$$

Since from equation (26.5), $(\partial S/\partial T)_v = C_v/T$

$$S = \int_0^T C_v \frac{dT}{T} = \int_0^T \frac{1}{T} \frac{\partial}{\partial T} \left[kT^2 \left(\frac{\partial}{\partial T} \ln \sum_i e^{-E_i/kT} \right)_v \right] dT \quad (54.12)$$

$$= \frac{1}{T} kT^2 \frac{\partial}{\partial T} \ln \sum_i e^{-E_i/kT} + \int_0^T \frac{kT^2}{T^2} \frac{\partial}{\partial T} \left(\ln \sum_i e^{-E_i/kT} \right) dT. \quad (54.13)$$

(55) The Helmholtz Free Energy and the Partition Function: From the relation, $F = A + pv$ there results, for one mole of an ideal gas. $A = F - RT$. In terms of the partition function this becomes:

$$A = -kT(N \ln f - N \ln N + N)$$

$$= -kT \left(N \ln f - N \ln \frac{N}{e} \right)$$

$$= -kT(N \ln f - \ln N!)$$

$$= -kT \ln \frac{f^N}{N!} \tag{55.1}$$

Assuming that $S = 0$ at $T = 0$ (Third Law).

$$S = kT \frac{\partial}{\partial T} \ln \sum_i e^{-E_i/kT} + k \ln \left(\sum_i e^{-E_i/kT} \right). \tag{54.14}$$

Now since $S = (E - A)/T$ and since the first term of equation (54.14) is actually E/T it follows directly from the second term of the expression that

$$A = -kT \ln \left(\sum_i e^{-E_i/kT} \right). \tag{54.15}$$

For a system containing one mole or the Avogadro number, N, like molecules, this expression becomes

$$A = -kT \ln \frac{f^N}{N!}. \tag{54.16}$$

where the $N!$ in the denominator takes account of the fact that the N molecules are indistinguishable from one another, $N!$ being therefore the number of indistinguishable configurations of N identical molecules in space, and partaking of the nature of a symmetry number (see Section 59). The expression so derived for A has complete generality whereas the derivation in the body of the text is limited in the case of F, and therefore in the case of A, to an ideal gas. Since $F = A + pv$ the general expression for F becomes, therefore,

$$F = -kT \ln \frac{f^N}{N!} + pv. \tag{54.17}$$

In the case of one mole of an ideal gas,

$$F = -kT \ln \frac{f^N}{N!} + RT. \tag{54.18}$$

Since $RT = RT \ln e$ and $N! = N^N e^{-N}$

$$F = -kT \ln \frac{f^N e^N}{N^N e^N} \tag{54.19}$$

$$= -kT \ln \frac{f^N}{N^N} \tag{54.20}$$

$$= -NkT \ln \frac{f}{N} \tag{54.21}$$

$$= -RT \ln \frac{f}{N}. \tag{54.22}$$

(56) **Entropy and the Partition Function:** From the thermodynamic relation $A = E - TS$, it follows that the expression for the entropy may be written thus:

$$S = \frac{E - A}{T} = NkT \left(\frac{\partial \ln f}{\partial T} \right)_v + k \ln f^N / N! \tag{56.1}$$

The same expression results from the thermodynamic relationship,

$$(\partial A / \partial T)_v = - S.$$

(57) **Partition Functions for Molecules:** In evaluating the partition function for a molecule consideration must be given to the several forms of energy which the molecule may possess, translational, vibrational, rotational and electronic. Each energy level of a molecule may be identified by assigning to it four quantum numbers, one for each type of energy. The partition function thus becomes

$$F = \sum_{t,r,v,e} e^{-E_{t,r,v,e}/kT}, \tag{57.1}$$

the summation being extended over all possible combinations of the quantum numbers. In the majority of cases our knowledge of these energy levels is not sufficient to carry through the summation exactly, so that approximations are, in practice, often employed.

To a good approximation the energy may be expressed as a sum of the energies of each type, in which case

$$E_{t,r,v,e} \approx E_t + E_r + E_v + E_e. \tag{57.2}$$

The partition function, to this approximation, becomes

$$f = \sum_{t,r,v,e} e^{-(E_t + E_r + E_v + E_e)/kT}$$

$$= \sum_t e^{-E_t/kT} \sum_r e^{-E_r/kT} \sum_v e^{-E_v/kT} \sum_e e^{-E_e/kT} = f_t f_r f_v f_e. \tag{57.3}$$

The evaluation of the partition function for any molecule depends therefore on knowledge of the energy levels, which are known either experimentally from the data of spectroscopy or theoretically from a quantum mechanical treatment of the molecule. The detailed examination of this phase of the subject will be presented in Chapter IV. When the exact data are lacking or when approximate solutions are sufficient, use is made of approximate partition functions for the several energies of the molecule and these are inserted in the expression (57.3) above.

(58) **Approximate Partition Function for Translational Motion:** According to quantum mechanics, for a particle of mass, m, moving in a box with edges of length a, b, c, the energy levels are

$$E_{p,q,r} = \frac{h^2}{8m} \left\{ \frac{p^2}{a^2} + \frac{q^2}{b^2} + \frac{r^2}{c^2} \right\}, \tag{58.1}$$

where p, q and r are integers. The partition function for translational motion thus becomes:

$$f_t = \sum_{p=1}^{\infty} e^{-p^2 h^2/8ma^2 kT} \sum_{q=1}^{\infty} e^{-q^2 h^2/8mb^2 kT} \sum_{r=1}^{\infty} e^{-r^2 h^2/8mc^2 kT}. \tag{58.2}$$

Since the exponential term $h^2/8ma^2kT$ and those corresponding for b and c are all much less than unity under ordinary conditions of temperature and volume, the summations may be replaced by integrations. Therefore, since

$$\int_0^{\infty} e^{-p^2 h^2/8ma^2 kT} \, dp = (2\pi mkT)^{1/2} a/h, \tag{58.3}$$

it follows that

$$f_t = \frac{(2\pi mkT)^{3/2} abc}{h^3} = \frac{(2\pi mkT)^{3/2} V}{h^3} , \tag{58.4}$$

where V is the volume of the box which thus enters the partition function of translation.

(59) **Approximate Partition Function for Rotational Motion:** For a linear molecule with moment of inertia, I, the rotational energy levels are

$$J(J + 1) \frac{h^2}{8\pi^2 I} \tag{59.1}$$

and there are $2J + 1$ states for each value of the energy. The partition function for rotation, f_r, becomes therefore

$$f_r = \sum_{J=0}^{\infty} (2J + 1) e^{-J(J+1) h^2/8\pi^2 I kT} \tag{59.2}$$

At high temperatures, the summation may be replaced by an integral, so that

$$f_r = \frac{8\pi^2 I kT}{h^2} . \tag{59.3}$$

For the case in which the two halves of the molecule are identical, the quantum mechanical treatment shows that only alternate values of J are allowed. The partition function is, therefore, obtained by a summation over half the levels only, and gives

$$f_r = \frac{8\pi^2 I kT}{2h^2} . \tag{59.4}$$

In general, for a linear molecule, the expression becomes

$$f_r = \frac{8\pi^2 I kT}{\sigma h^2} , \tag{59.5}$$

where the symmetry number σ is 2 if both halves of the molecule are alike and otherwise σ is unity. The symmetry number is the number of equivalent ways of orienting the molecule.

For a non-linear molecule with principal moments of inertia, A, B and C, a corresponding development gives

$$f_r = \frac{8\pi^2 (8\pi^3 ABC)^{1/2} (kT)^{3/2}}{\sigma h^3} . \tag{59.6}$$

The symmetry number, σ, is again determined by the number of equivalent ways of orienting the molecule in space as can be seen from the following values: $\sigma_{H_2O} = 2$; $\sigma_{NH_3} = 3$; $\sigma_{C_2H_4} = 4$; $\sigma_{CH_4} = 12$; $\sigma_{C_6H_6} = 12$.

(60) **Approximate Partition Function for Vibrational Motion:** A molecule containing n atoms has $3n - 6$ vibrational degrees of freedom if it is non-linear, and $3n - 5$ if it is linear. Each vibrational degree of freedom may be considered as an harmonic oscillator. The partition function for such an oscillator has already been given in Case 1, Section 49, as

$$f_r = (1 - e^{-h\nu_i/kT})^{-1}. \tag{60.1}$$

For i vibrational degrees of freedom the approximate partition function for vibrational motion becomes:

$$f_v = \prod_{i=1}^{i=3n-x} (1 - e^{-h\nu_i/kT})^{-1}, \tag{60.2}$$

where the required frequencies, ν_i, are obtained from infra-red and Raman spectra of the molecule.

(61) **Partition Function for Electronic Energy:** This function is directly calculated from the observed electronic energy levels of the molecule using the relation

$$f_e = \sum_e g_e e^{-E_e/kT}. \tag{61.1}$$

In chemical reactions, the electronic energy levels are in general too high in energy above the ground state to contribute materially to the partition function at ordinary temperatures. Most diatomic molecules have $^1\Sigma$ ground states and the electronic partition function is usually unity. For molecules having multiplet ground states, such as nitric oxide, oxygen and the hydroxyl radical this partition function must be suitably modified. It is especially to be remembered that a multiplet ground state modifies correspondingly the rotational partition function, replacing the single energy level by a multiplicity of levels.

(62) **Gas Pressure and the Partition Function:** As an example of the applicability of the partition function, the pressure of a gas composed of non-linear molecules can be calculated. From the preceding it is evident that, ignoring electronic energy levels, the partition function for such an n-atomic

molecule becomes

$$f = \frac{(2\pi m k T)^{3/2}}{h^3} v \frac{8\pi^2 (8\pi^3 A B C)^{3/2}}{h^3} \prod_{i=1}^{i=3n-6} (1 - e^{-h\nu_i/kT})^{-1}. \qquad (62.1)$$

The partition function is a function of the mass, moments of inertia, frequencies of vibration, symmetry of the molecules, temperature and volume. From the thermodynamic relation, $p = -(\partial A/\partial v)_T$, it follows that, for an ideal gas,

$$p = kT \frac{\partial}{\partial v} \ln \frac{f^N}{N!} = NkT \frac{\partial}{\partial v} \ln f = \frac{NkT}{v}. \qquad (62.2)$$

For a gas obeying van der Waals's equation, with potential energy of interaction between the molecules, the translational partition function would be modified by the substitution for v of the term $v - b$ and multiplication of the function by $e^{a/vRT}$. The pressure so calculated would have the familiar form of the van der Waals equation.

(63) **Partition Functions for Liquids and Solids:** For these states of matter the translational and rotational terms disappear in the partition function and are replaced by vibrational terms in which the frequencies are functions of volume and temperature. There will also be an interaction term of the general form $e^{-E(v,T)/RT}$ analogous to the term $e^{a/vRT}$ of the van der Waals gas. The calculation of the partition function follows that for a gas when this interaction term has been introduced.

CHAPTER IV

THE THIRD LAW OF THERMODYNAMICS AND STATISTICAL MECHANICS

BY JOHN G. ASTON,

Director of the Cryogenic Laboratory and Professor of Organic Chemistry,
The Pennsylvania State College

(1) The inter-relations of the thermodynamic quantities, free energy F, heat content H and entropy S of a single molecular species are embodied in the equation of the first and second laws of thermodynamics

$$F = H - TS. \tag{1.1}$$

Applied to a chemical reaction among several species the equation becomes

$$\Delta F = \Delta H - T\Delta S, \tag{1.2}$$

where the respective symbols refer to increases in the respective thermodynamic magnitudes for reactants and products in specified states; in terms of the species at unit activity, i.e., in their standard states, the relation may be written

$$\Delta F^0 = \Delta H^0 - T\Delta S^0, \tag{1.3}$$

in which case the standard free energy is related to the equilibrium constant K by the expression

$$\Delta F^0 = -RT \ln K. \tag{1.4}$$

The position of equilibrium may therefore be calculated from calorimetric heats of reaction at constant pressure, which yield ΔH^0, if the entropy change can be readily obtained. It is the purpose of the present chapter to examine methods of obtaining the entropy change in chemical processes. It will be shown that in contradistinction to the thermodynamic quantities F and H, absolute values of the entropy S of substances are attainable and may be independently determined. This was essentially the problem which G. N. Lewis,[1] Richards,[2] van't Hoff,[3] Haber,[4] Nernst,[5] and Planck [6] attempted to solve and

---

[1] G. N. Lewis, *Proc. Am. Acad.*, **35**, 3 (1899).

[2] Richards, *Z. physik. Chem.*, **42**, 129 (1902).

[3] van't Hoff, Boltzmann Festschrift, p. 233, Barth, Leipzig (1904).

[4] Haber, Thermodynamik technischer Gasreaktionen, Oldenbourg, Munich, 1905.

[5] Nernst, *Nachr. kgl. Ges. Wiss. Göttingen, Math.-Phys. Klasse*, 1 (1906). Die theoretischen und experimentallen Grundlagen des neuen Wärmesatzes, Halle (1918).

[6] Planck, *Ber.*, **45**, 5 (1912).

their efforts have led to a solution which is embodied in the Third Law of Thermodynamics. The famous Nernst Heat Theorem was the first practical solution to the problem. This theorem *assumed* that the entropy per gram atom was the same for all condensed phases at the absolute zero and that near the absolute zero the change in heat capacity at constant pressure, ΔC_p, approached zero asymptotically. Nernst's method expressed the equilibrium constant in terms of the so-called "chemical constants" of each of the reactants and products of the reaction. The direct use of these "chemical constants" is becoming less prevalent; hence, Nernst's method will be postponed until the end of the chapter and then developed in terms of modern ideas.

THE THIRD LAW OF THERMODYNAMICS

(2) The quantum hypothesis and the relation of entropy to probability, which is to be discussed presently, lead to the conclusion that the entropy of all "perfect" crystals at the absolute zero is the same. Moreover, this limiting value is the lowest attainable value for the entropy so that we take it as zero. By "perfect" is meant a geometrical arrangement of atoms which is repeated *without modification* throughout the crystal. Whenever it is possible to obtain a perfect crystal of an element or compound at low temperatures, this postulate allows us to obtain the entropy of the compound in any state at any temperature experimentally.

(3) **Entropy from Calorimetric Data:** For constant pressure conditions the general equation

$$dS = \frac{q}{T},\qquad (3.1)$$

where q is the heat absorbed in any infinitesimal reversible change at the temperature T, becomes

$$dS = \frac{dH}{T}.\qquad (3.2)$$

Integration then gives

$$S = \int_0^T \frac{dH}{T} + S_0,\qquad (3.3)$$

where S_0 is the entropy of the substance at the absolute zero and S that at the temperature T. If the substance is in the "perfect crystalline state" at the absolute zero, S_0 is zero and equation (3.3) can be expanded into the form

$$S = \int_0^{T'} \frac{C_p}{T}\,dT + \frac{\Delta H'}{T'} + \int_{T'}^{T''} \frac{C_p}{T}\,dT + \frac{\Delta H''}{T''} + \int_{T''}^{T'''} \frac{C_p}{T}\,dT + \cdots,\qquad (3.4)$$

where C_p is the heat capacity at constant pressure. The first term is an integral taken over the range from the absolute zero to the first transition point, if any, of the crystal and is the entropy increase in the crystal in going from the absolute zero to this transition point. The second term is the entropy of

transition. The third term is the increase in entropy from the first to the second transition and so on. Thus, if the entropy of the gas at the normal boiling point is desired, this process is carried on so as to include the transitions from solid to liquid (fusion) and liquid to gas at one atmosphere (vaporization).

The heat capacities at constant pressure and heats of transition, including fusion and vaporization are readily measured from about 10° K upwards. The heat capacity of crystalline substances is very small at 10° K and only a small extrapolation is required in evaluating the first term of equation (3.4). This extrapolation will be discussed shortly. For the present we will state that, with sufficient accuracy (0.05 cal. per deg.), the entropy of the crystal below a temperature T near 10° K is given by $(C_p)_T/3$, where $(C_p)_T$ is the heat capacity of the crystal at the temperature T. The first term in equation (3.4) then becomes

$$\int_0^{T'} \frac{C_p}{T} \, dT = \frac{(C_p)_T}{3} + \int_T^{T'} \frac{C_p}{T} \, dT. \tag{3.5}$$

The last integral is easily obtained graphically by plotting C_p against $\ln T$ and taking the area under the curve between the required values of $\ln T$.

TABLE 1

THE ENTROPY OF HYDROGEN CHLORIDE FROM CALORIMETRIC DATA

Solid Stable Below 98.36° K	Cal./Deg./Mole
0 to 16° K, extrapolation..	0.30
16 to 98.36° K, graphical..	7.06
Transition 284.3/98.36........	2.89
Solid Stable Above 98.36° K	
98.36 to 158.91° K, graphical..	5.05
Fusion, 476.0/158.91.......	3.00
Liquid	
158.91 to 188.07° K, graphical ..	2.36
Vaporization, 3860/188.07.....	20.52
Entropy of HCl gas at boiling point .	41.2 ± 0.1 E.U.
Correction for gas imperfection ..	0.10
Entropy of ideal HCl gas at boiling point...	41.3

Entropy of ideal HCl gas at boiling point from Spectroscopic Data 41.45

Table I is an example of such a calculation for hydrogen chloride.[1] The heat capacity data on which the calculations are based are shown in Fig. 1. The first entry in the table is the extrapolation below 16° K; the third and fifth are the entropies of transition and fusion, respectively. The transition occurs at 98.36° K and the heat of transition is 284.3 cal. per mole. The quotient indicated in the table is the entropy of transition. Similar terms are introduced for fusion and vaporization.

[1] Giauque and Wiebe, *J. Am. Chem. Soc.*, **51**, 101 (1928).

The first total in Table I is the entropy of the actual gas at one atmosphere (*S*). For comparison with entropies from spectroscopic data we require the entropy of the ideal gas at one atmosphere (S^0), i.e., in the so-called standard state. This is also the entropy to be used in conjunction with the free energy
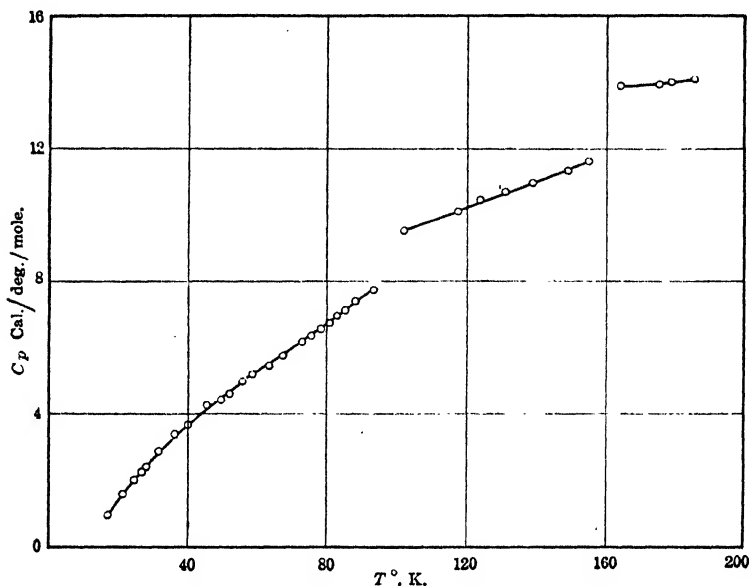
Fig. 1. Heat Capacity (Cal./Deg./Mole) of Hydrogen Chloride

of the gas in the standard state. The expression for obtaining S^0 from S is

$$S^0 = S - \int_0^P \left[\left(\frac{\partial V}{\partial T} \right)_P - \frac{R}{P} \right] dP. \tag{3.6}$$

If the gas is assumed to obey the modified Berthelot equation of state, namely

$$PV = RT \left[1 + \frac{9PT_c}{128P_cT} \left(1 - 6\frac{T_c^2}{T^2} \right) \right],$$

then

$$S^0 = S + \frac{27}{32} \cdot \frac{RT_c^3 P}{T^3 P_c} . \tag{3.7}$$

The second total in Table I is S^0 obtained by adding the last term in equation (3.7) to the first total.

(4) **The Nature of the Extrapolation to the Absolute Zero:** There is much in the early literature about the value of $\int C_p \, d \ln T$ from the absolute zero to the lowest temperature attainable. Before the application of quantum theory

to the specific heats of solids, the possibility was considered that C_p might have a finite value at temperatures infinitesimally close to the absolute zero. Were this true, the value of this integral might reach very large values and be infinite if C_p were finite at the absolute zero. Moreover, the experimental data might be such that C_p had fallen to small values and given the impression of an asymptotic approach to zero which actually did not exist. The work of Einstein and Debye on the application of quantum theory to the specific heat of crystalline solids, to be described later, now leaves no doubt that perfect crystals, of which most substances at low temperatures are examples, approach zero asymptotically near the absolute zero; the derivation of equation (3.5) is thus possible.

Restricted Statement of the Third Law: The statement that the entropy of all "perfect" crystals is zero at the absolute zero while their heat capacities (C_p) approach zero asymptotically near the absolute zero is a somewhat restricted statement of *the third law of thermodynamics*.

(5) **Methods of Checking the Third Law:** There are four methods of checking the third law:

(a) The entropy of a crystalline compound, capable of existing in two crystalline forms, is measured at some temperature above the transition temperature by following two paths. (a) By rapid cooling, the metastable high temperature form is obtained at 10° K and the heat capacities of this form are measured up to the desired temperature. The entropy at this temperature is calculated using equations (3.4) and (3.5). (b) By slow cooling the equilibrium form of the crystal is obtained at 10° K. The heat capacities of this form are measured up to the transition temperature together with the heat of transition to the high temperature form. The entropy of the high temperature form is then calculated at the same temperature as in (a) using (3.4) and (3.5). If both crystalline forms are perfect at 10° K, and the third law is correct, the same value of the entropy should be obtained by both methods.

This method of checking the third law has been applied to cyclohexanol [1] and to phosphine [2] with a high degree of accuracy. Table II summarizes the

TABLE II

THE ENTROPY OF PHOSPHINE FROM THE THIRD LAW OF THERMODYNAMICS

Form stable below 49.43° K	Cal./Deg./Mole	Form stable above 49.43° K	Cal./Deg./Mole
0–15° K extrapolation	0.338	0–15° K extrapolation	0.495
15–49.43° K (graphical)	4.041	15–30.29° K (graphical)	2.185
Transition $\beta \rightarrow \alpha$ 185.7/49.43	3.757	Transition $\gamma \rightarrow \alpha$ 19.6/30.29	0.647
		30.29–49.43° K (graphical)	4.800
	8.14		8.13

calculation, by two paths, of the entropy at the transition temperature of the form of phosphine (α-modification) stable above 49.43° K, after the transition

[1] Kelley, *J. Am. Chem. Soc.*, **51**, 1400 (1929).
[2] Stephenson and Giauque, *J. Chem. Phys.*, **5**, 149 (1937).

has occurred. In the first of these methods of calculation, the compound was cooled slowly, thus allowing transition to the crystalline modification stable below 49.43°K (β-modification). The specific heat measurements were started at 15° K thus obtaining $\int C_p \, d \ln T$ for the temperature range 15° to 49.43° K. The heat absorbed in the transition was 185.7 calories per mole and therefore the entropy of transition was 185.7/49.43 = 3.757. The sum of this quantity and the integral together with the extrapolated entropy from 0° to 15° K yield a value for the entropy of the form stable above 49.43° K at the transition point. This calculation is recorded in the first column of Table II.
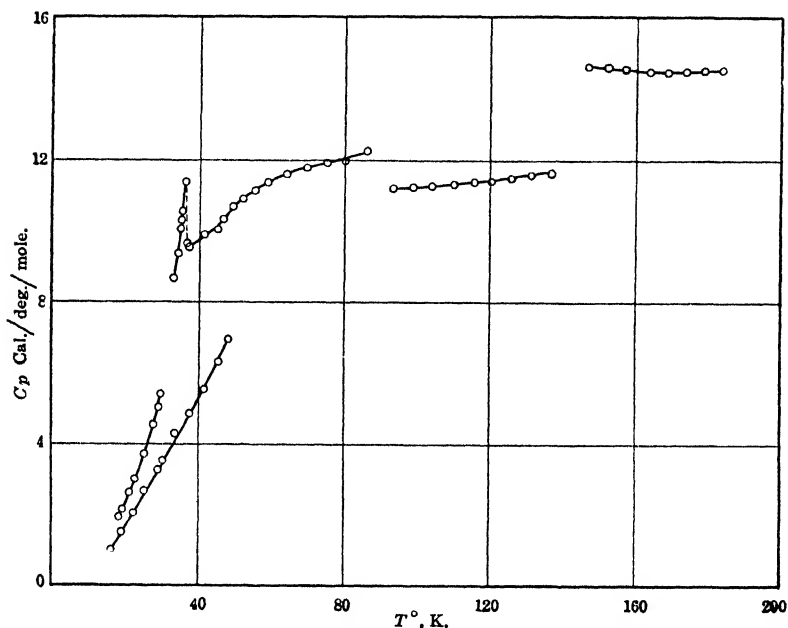
Fig. 2. Heat Capacity (Cal./Deg./Mole) of the Forms of Phosphine

For the second method of calculation the form stable above 49.43° K was cooled rapidly, thus obtaining this modification in a pure state down to 30.29° K. At this point, a different transition occurred to a third crystalline variety (γ-modification) which was cooled to 15° K. The second column in Table II shows the thermal data up to 49.43° K, including the entropy of the metastable transition to the form stable above 49.43° K of which the heat of transition is 19.6 calories per mole. The sum of the terms gives a second and independent value of the entropy at the transition point of the form stable above 49.43° K. The first method gives 8.13 cal./deg./mole and the second method 8.14 cal./deg./mole. This could only be true if the γ-modification had the same entropy at the absolute zero as the β-modification. Fig. 2 shows the heat capacities of the system on heating from 15° K by the two paths.

The results with cyclohexanol are of the same nature; this substance has a transition at 263.5° K, but the form stable above 263.5° K (α-modification) can be supercooled down to 13.5° K without transition. The heat capacities of the α-form yield an entropy value at the transition point of 41.2 ± 0.25 cal./deg./mole. When the transition to the β-modification is allowed to occur by slow cooling, the heat capacities obtained for the β-modification, together with the heat of transition (1960 calories per mole), yield a value of the entropy of the β-form at the transition point of 40.90 ± 0.25 cal./deg./mole. The difference of 0.3 cal./deg./mole is well within the experimental error and indicates that both forms have the same entropy at the absolute zero.

(*b*) For a chemical reaction

$$aA + bB = mM + nN$$
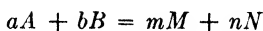
the molal entropy of each of the reactants and products in their standard states (S^0) is determined from the thermal data using equations (3.4) and (3.5) at some temperature where the equilibrium constant of the reaction can be determined. The value of ΔS^0 calculated from the individual entropies is then compared with the one obtained from the equilibrium constant and the heat of reaction (ΔH^0) using equations (1.3) and (1.4). Alternatively, if the reaction can be made to occur in a cell, the temperature coefficient of the electromotive force of the cell will give a value of ΔS^0 directly (Chap. III). Agreement should be obtained if the third law is valid and the individual substances are perfect crystals at low temperatures.

The application of the second method is not as definite as that of the first for two reasons. The accurate measurement of an equilibrium constant is not an easy matter and accurate heat of reaction measurements are rare; also, some common chemical substances, including hydrogen and water, do not form perfect crystals at low temperatures and do not have zero entropy at the absolute zero. The reason for this zero point entropy is well understood and will be discussed presently. In such a case the entropy, calculated with the aid of statistical mechanics, can be used instead of the third law value, together with the third law values for the other participants in the reaction, to obtain ΔS for the process. The statistical mechanical treatment is discussed later. In Table III examples of the method are given in which purely third law values are used. Column 1 gives the chemical equation for the reaction, column 2 gives the temperature, column 3 gives the values of ΔS obtained using the third law, column 4 gives the values of ΔS obtained using equations (1.3) and (1.4) (the equilibrium data) or using the temperature coefficient of electromotive force.

The first three reactions in Table III provide excellent confirmation of the third law. The results for the dehydration of magnesium hydroxide appear less satisfactory; the third law value of ΔS^0 is 0.82 cal./deg./mole lower than the value from the equilibrium data. It will be shown later that there is 0.806 cal./deg./mole residual entropy in crystalline water due to lack of per-

TABLE III

CHECKS OF THE THIRD LAW OF THERMODYNAMICS

Reaction	Temp. °K	ΔS Third Law [1] Cal./Deg./Mole	ΔS Experimental
$Ag(s) + \frac{1}{2}Br_2(l) = AgBr(s)$	265.9	-3.01 ± 0.40	-3.13 ± 0.10 * -3.02 ± 0.10 *
$Ag(s) + \frac{1}{2}Cl_2(g) = AgCl(s)$	298.16	-13.85 ± 0.25	-13.73 ± 0.10 *
$Zn(s) + \frac{1}{2}O_2(g) = ZnO(s)$	298.16	-24.07 ± 0.25	-24.24 ± 0.05 †
$Mg(OH)_2(s) = MgO(s) + H_2O(g)$	298.16	35.85 ± 0.08	36.67 ± 0.10 †

* From E.M.F. measurements.

† From ΔH and equilibrium constant.

[1] References to entropy values:

(a) $Ag(s)$, Eucken, Clusius and Woitinek, *Z. anorg. Chem.*, **203**, 39 (1931).

(b) $Br_2(l)$, Latimer and Hoenshel, *J. Am. Chem. Soc.*, **48**, 19 (1926).

(c) $Cl_2(g)$, Giauque and Powell, *ibid.*, **61**, 1970 (1939).

(d) $Zn(s)$, Kelley, *Bureau of Mines Bulletin*, 350, page 43 (1932).

(e) $O_2(g)$, Giauque and Johnston, *J. Am. Chem. Soc.*, **51**, 2300 (1929).

(f) $ZnO(s)$, see reference (d).

(g) $MgO(s)$, Giauque and Archibald, *J. Am. Chem. Soc.*, **59**, 561 (1937).

(h) $Mg(OH)_2(s)$, see reference (g).

(i) $H_2O(g)$, Giauque and Stout, *ibid.*, **58**, 1144 (1936).

(j) $AgBr(s)$, Clusius and Harteck, *Z. phys. Chem.*, **A**, **134**, 243 (1928).

(k) $AgCl(s)$, Eastman and Milner, *J. Chem. Phys.*, **1**, 444 (1933).

(l) $Ag(s) + \frac{1}{2}Br_2(l) = AgBr(s)$, see reference (a).

(m) $Ag(s) + \frac{1}{2}Cl_2(g) = AgCl(s)$, Gerke, *J. Am. Chem. Soc.*, **44**, 1684 (1922).

(n) $Zn(s) + \frac{1}{2}O_2(g) = ZnO(s)$, Kelley, *Bureau of Mines Bulletin*, 324, pages 21–24 (1930).

(o) $Mg(OH)_2(s) + MgO(s) = H_2O(g)$, see reference (g).

fection in the crystal; this would make ΔS^0 for the reaction an equal amount lower than that obtained from the equilibrium data. The observed difference of 0.82 E.U. is in close agreement.

The entropy of many aqueous ions has been calculated by Latimer and co-workers from a combination of third law entropies, or statistical mechanical entropies, with the entropy changes in chemical reactions. Often more than one value of the entropy of a particular ion has been calculated by this method, using different steps. Table IV lists these entropies in such a way as to show their relation to the third law entropies. Column 2 gives the third law entropy of the salt listed in column 1. This entropy is needed, in addition to that of the other salts or ions given above it in the table, in order to obtain the entropy of the ion named in column 5 from the entropy change in the reaction listed in column 3. Column 4 gives the entropy change in the reaction and column 6 the entropy of the ion. The references to the third law entropies and the final values for the ions are given in the footnotes. The symbol (i) after an ion indicates there is another value lower in the table; the symbol (ii) indicates that the value is the second one in the table with another yet to follow, unless it is

TABLE IV

IONIC ENTROPIES BASED ON THE THIRD LAW AND OTHER DATA

Salt	$S^0_{298.15}$	Reaction	$\Delta S_{298.15}$	Ion	$S^0_{298.15}$
$H_2O(l)$ [1]	16.77				
$Ag_2O(s)$ [2]	29.05	$Ag_2O + 2H^+ = 2Ag^+ + H_2O(l)$	22.58	Ag^+(i)	17.46 [2]
$HCl(g)$ [3]	44.66	$HCl(g) = H^+ + Cl^-$	−31.14	Cl^-	13.52 [4]
$AgCl(s)$ [3]	23.0	$AgCl(s) = Ag^+ + Cl^-$	8.15	Ag^+(ii)*	17.62 [4]
$AgBr(s)$ [3]	25.6	$AgBr(s) + Cl^- = AgCl(s) + Br^-$	3.69	Br^-	19.8 [4]
$Ag_2SO_4(s)$ [5]	47.76	$Ag_2SO_4(s) = 2Ag^+ + SO_4^-$	−8.3	SO_4^-(i)	2.8 [5]
$AgIO_3(s)$ [6]	36.0	$AgIO_3(s) = Ag^+ + IO_3^-$	10.1	IO_3^-(i)	34.3 [6]
$KCl(s)$ [3]	19.76	$KCl(s) = K^+ + Cl^-$	17.96	K^+(i)	24.2 [4]
$KBr(s)$ [3]	22.4	$KBr(s) = K^+ + Br^-$	21.4	K^+(ii)*	24.3 [4]
$KClO_4(s)$ [7]	36.1	$KClO_4(s) = K^+ + ClO_4^-$	31.7	ClO_4^-	46.2 [7]
$KClO_3(s)$ [8]	34.17	$KClO_3(s) = K^+ + ClO_3^-$	29.4	ClO_3^-	34.3 [8]
$KBrO_3(s)$ [9]	35.65	$KBrO_3(s) = K^+ + BrO_3^-$	27.2	BrO_3^-(i)	37.4 [9]
$KIO_3(s)$ [9]	36.20	$KIO_3(s) = K^+ + IO_3^-$	15.9	IO_3^-(ii)*	26.9 [9]
$KNO_3(s)$ [3]	31.8	$KNO_3(s) = K^+ + NO_3^-$	27.4	NO_3^-(i)	35.0 [4]
$NaCl(s)$ [3]	17.3	$NaCl(s) = Na^+ + Cl^-$	10.4	Na^+(i)	14.1 [4]
$NaNO_3(s)$ [10]	23.8	$NaNO_3(s) = Na^+ + NO_3^-$	21.5	Na^+(ii)*	14.3 [10]
$Na_2SO_4 \cdot 10H_2O(s)$ [3]	142.8	$Na_2SO_4 \cdot 10H_2O(s) = 2Na^+ + SO_4^- + 10H_2O(l)$	57.7	SO_4^-(ii)	4.4 [4]
$RbClO_3(s)$ [3]	34.2	$RbClO_3(s) = Rb^+ + ClO_3^-$	32.0	Rb^+(i)	28.9 [4]
$RbClO_4(s)$ [3]	41.1	$RbClO_4(s) = Rb^+ + ClO_4^-$	33.6	Rb^+(ii)*	28.5 [4]
$CsClO_4(s)$ [3]	44.5	$CsClO_4(s) = Cs^+ + ClO_4^-$	33.5	Cs^+	31.8 [4]
$CsAl(SO_4)_2 \cdot 12H_2O(s)$ [11]	163.0	$CsAl(SO_4)_2 \cdot 12H_2O = Cs^+ + Al^{+++} + 2SO_4^- + 12H_2O(l)$	2	Al^{+++}	−76 [11]
$BaCl_2 \cdot 2H_2O(s)$ [12]	45.58	$BaCl_2 \cdot 2H_2O = Ba^{++} + 2Cl^- + 2H_2O(l)$	14.2	Ba^{++}	2.2 [12]
$Ba(BrO_3)_2 \cdot H_2O(s)$ [13]	80.72	$Ba(BrO_3)_2 \cdot H_2O = Ba^{++} + 2BrO_3^- + H_2O(l)$	26.5	BrO_3^-(ii)*	43.6 [13]
$BaSO_4(s)$ [14]	31.51	$BaSO_4 = Ba^{++} + SO_4^-$	26.3	SO_4^-(iii)	3.0 [14]
$Ba(NO_3)_2(s)$ [3]	51.1	$Ba(NO_3)_2(s) = Ba^{++} + 2NO_3^-$	21.1	NO_3^-(ii)*	35.0 [4]
$CO_2(g)$ [3]	51.08				
$CaCO_3(s)$ [3]	22.2	$CaCO_3 + 2H^+ = Ca^{++} + H_2O(l) + CO_2$	34.2	Ca^{++}	−11.4 [4]
$CaSO_4 \cdot 2H_2O(s)$ [14]	46.36	$CaSO_4 \cdot 2H_2O(s) = Ca^{++} + SO_4^- + 2H_2O(l)$	−21.8	SO_4^-(iiii)*	3.8 [14]
$CaC_2O_4 \cdot 2H_2O(s)$ [15]	37.28	$CaC_2O_4 \cdot 2H_2O(s) = Ca^{++} + C_2O_4^- + 2H_2O(l)$	−22.5	$C_2O_4^-$	9.3 [15]

[1] Gordon, *J. Chem. Phys.*, **2**, 65 (1934).

[2] Pitzer and Smith, *J. Am. Chem. Soc.*, **59**, 2633 (1937).

[3] Kelley, *Bureau of Mines Bulletin*, 394 (1935).

[4] Latimer, Pitzer and Smith, *J. Am. Chem. Soc.*, **60**, 1829 (1938).

[5] Latimer, Hicks and Schutz, *J. Chem. Phys.*, **1**, 424 (1933).

[6] Greensfelder and Latimer, *J. Am. Chem. Soc.*, **53**, 3813 (1931).

[7] Latimer and Ahlberg, *ibid.*, **52**, 552 (1930).

[8] Latimer, Schutz and Hicks, *ibid.*, **56**, 88 (1934).

[9] Ahlberg and Latimer, *ibid.*, **56**, 856 (1934).

[10] Brown, Smith and Latimer, *ibid.*, **59**, 921 (1937).

[11] Latimer and Greensfelder, *ibid.*, **50**, 2202 (1928).

[12] Brown, Smith and Latimer, *ibid.*, **58**, 1758 (1936).

[13] Greensfelder and Latimer, *ibid.*, **50**, 3286 (1928).

[14] Latimer, Hicks and Schutz, *J. Chem. Phys.*, **1**, 620 (1933).

[15] Latimer, Schutz and Hicks, *J. Am. Chem. Soc.*, **55**, 971 (1933).

marked by an asterisk, representing the last value to be given for the ion in the table.

In Table V the several values of each ionic entropy with more than one value are listed together for comparison. The agreement obtained constitutes an excellent test of the third law of thermodynamics.

TABLE V

COMPARISON OF IONIC ENTROPIES AT 298.15° K AS A TEST OF THE THIRD LAW

Ion	$S^0_{298.15}$ (Cal./Deg./Mole)			
	(i)	(ii)	(iii)	(iiii)
Ag⁺... .	17.46	17.62		
SO₄⁻. . ..	2.8	4.4	3.0	3.8
IO₃⁻. .	34.3	26.9		
K⁺..... ..	24.2	24.3		
BrO₃⁻. .	37.4	43.6		
NO₃⁻..	35.0	35.0		
Na⁺..........	14.1	14.3		
Rb⁺..........	28.9	28.5		

(c) By the use of statistical mechanics and principles which are consistent with the third law, the entropy of a gas can be calculated if the molecular energy levels are known. A test of the third law is possible from a comparison of this value of the entropy with one obtained using calorimetric data for the substance to low temperatures and the postulates of the third law of thermodynamics.

(d) A fourth method verifies the fact that the entropy of all perfect crystals is the same (zero) at the absolute zero independently of any other variables. Consider the equation

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P, \tag{5.1}$$

then if the entropy of a perfect crystal is zero at the absolute zero at all pressures

$$\left(\frac{\partial S}{\partial P}\right)_T = 0 \quad \text{and} \left(\frac{\partial V}{\partial T}\right)_P = 0. \tag{5.2}$$

It has been found experimentally that $(\partial V/\partial T)$ approaches zero at the absolute zero for all crystalline substances examined: these include copper,[1] aluminum and silver[2] investigated down to −250°, and also diamond, sodium chloride, silicon dioxide, calcium fluoride and FeS_2 studied down to −180°.[3]

[1] Keesom, van Agt and Jansen, *Proc. Roy. Soc. Amsterdam*, **29**, 786 (1926).

[2] Ebert, *Z. Physik*, **47**, 712 (1928).

[3] Buffington and Latimer, *J. Am. Chem. Soc.*, **48**, 2305 (1926).

It will be shown later that the temperature coefficient of the magnetic susceptibility should reach zero at the absolute zero; there is every reason to believe that such is the case.

(6) **Concerning the Coordinates Used:** It is convenient to consider a system containing only one kind of molecule; the results obtained can then readily be extended to systems containing several kinds. Let this system contain n molecules and let each of these molecules contain a atoms. It requires three coordinates to specify the position of each atom so that $r = 3a$ quantities (coordinates in a general sense) are required to specify the exact position of the molecule. These may be the a sets of Cartesian coordinates belonging to the atoms (x_i, y_i, z_i) but such a system is not convenient and simplicity is gained by using the following one.

The center of gravity of the molecule is fixed by the Cartesian coordinates $\bar{x}, \bar{y}, \bar{z}$. The orientation of the molecules is fixed by the system of three angles which orients the common type of geographic globe. In this system (see Fig. 3) three fixed axes at right angles x', y' and z' are chosen in the molecule and their position referred to three axes x, y and z fixed in space (these can be the same as those which are used to define the center of gravity). The axis z' may be regarded as a polar axis, which is oriented by giving the angle, θ, between it and the axis z. To fix completely the orientation of the axis z' requires one more angle ψ. This is taken as the angle between the fixed x axis and the line ON, in which the $x'y'$ plane intersects the xy plane, called the nodal line. The

FIG. 3. Eulerian Angles

orientation of the molecule is then specified completely by giving the angle ϕ that x' makes with the nodal line. The angles θ, ψ and ϕ are called the *Eulerian angles*.

There still remain $3a - 6$ quantities to be specified to define completely the state of the molecule: these are the internal coordinates. If there are b internally rotating groups within the molecule, their position can be specified by b angles ω_1, ω_2, $\cdots \omega_b$ which define the positions of radius vectors at right angles to the respective axes of rotation. The $3a - 6 - b$ quantities still to be defined give the relative positions of atoms, the centers of gravity of internally rotating groups and the relative positions of atoms within internally rotating groups. For these a set of axes fixed in the molecule with one of the atoms as origin is usually chosen, and the Cartesian coordinates with respect to these
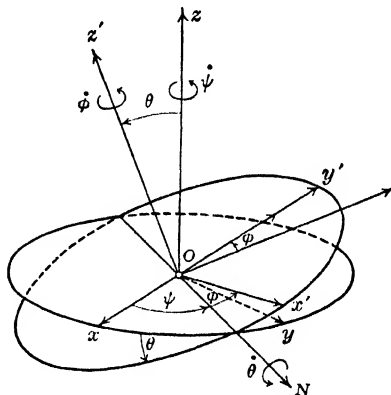
axes are then given for all the other atoms. In this way there are obtained $b + 3$ more quantities than are required; these are, however, variables which are dependent on the others.

The $3a = r$ coordinates thus defined are generalized coordinates. These will be denoted by $q_1, q_2, \cdots, q_r$ where the first three may be identified with $\bar{x}, \bar{y}$ and $\bar{z}$ while q_4, q_5 and q_6 denote θ, ψ and ϕ. A hyperspace of r dimensions may be imagined and in it the exact configuration of the molecule is then specified by laying off the quantities $q_1, \cdots, q_r$ along r mutually perpendicular axes, thus defining a point. Such a specification gives only the instantaneous position of the molecule but does not tell how it is moving. To define the motion, a further r quantities must be given, namely, the r generalized momenta $p_1, \cdots, p_r$ corresponding to the generalized coordinates. The exact mechanical condition of the molecule can be represented by a point in a hyperspace of $2r$ dimensions by plotting the quantities $q_1, \cdots, q_r, p_1, \cdots, p_r$ along $2r$ mutually perpendicular axes. This space, representing the mechanical state of a molecule, is very often referred to as the μ-space.

A system of n of these molecules has $3na = nr$ degrees of freedom, namely, the quantities $q_1, q_2, \cdots, q_r$ for each molecule. For example $q_1^1, q_2^1, \cdots, q_r^1$ for the first molecule $q_1^2, q_2^2, \cdots, q_r^2$ for the second and $q_1^i, q_2^i, \cdots, q_r^i$ for the ith molecule. The corresponding symbols $(p_1^i, \cdots, p_r^i)$ are used for the momenta.

The precise mechanical condition of the system can be defined by a point in a hyperspace of $2nr$ dimensions with $2nr$ rectangular axes, one for each of the quantities $q_1^1, \cdots, q_r^n, p_1^1, \cdots, p_r^n$. Such a space is known as the γ-space.

It is not necessary to know the exact mechanical condition of each molecule but merely that the quantities $q_1, \cdots, q_r, p_1, \cdots, p_r$ lie within limits smaller than the accuracy of any reasonable measurement. That is, it is sufficient to specify the mechanical condition of each molecule by placing it anywhere in a small volume element in the μ-space

$$\delta v_\mu = dq_1 \cdots dq_r \ dp_1 \cdots dp_r.$$

Such a volume element is spoken of as a "cell" in the μ-space.

For the system it is sufficient to know the mechanical condition (phase) within limits corresponding to the size of the cell taken for the molecule. A volume element in the γ-space

$$\delta v_\gamma = dq_1^1 \cdots dq_r^n \ dp_1^1 \cdots dp_r^n$$

defines the state of the system and to say that the system lies anywhere within this volume element defines it with sufficient accuracy for our purpose.

(7) **Microscopic and Macroscopic States:** An alternative definition of the state of the system can be given by specifying the index numbers of the molecules $(1, 2, 3, \cdots, n)$ whose mechanical condition corresponds to each cell in the μ-space. For this purpose an index number can be assigned to each cell. The state of the system is then ascertained by "taking stock" of the cells in the

μ-space, both with respect to the number and individuality (index number) of the molecules that each contains. It should be noted that, if the molecule denoted by the superscript i in one cell is interchanged for that denoted by the superscript j which is in another, a new state of the system is obtained. This is because there is a set of axes in the γ-space for each molecule and such an exchange has interchanged axes. For a three dimensional space an analogous change would be that which converts the point ($x = 1$, $y = 2$, $z = 3$) into the point ($x = 1$, $y = 3$, $z = 2$).

The state of the system defined in this way is called a *microscopic* state. Such a specification of the state of the system is required for the statistical treatment of the system, but it is much more detailed than is necessary to define the physical properties of the system. As far as the physical behavior of the system is concerned, it makes no difference if we interchange the co-ordinates and momenta of two identical molecules of index numbers i and j, i.e., exchange them between cells of the μ-space. To get a change in physical behavior the total number of molecules in at least two of the cells of the μ-space must be changed, i.e., the population of the cells in the μ-space must be changed. The state of the system, as defined by specifying the population of the cells in the μ-space without regard to identity of molecules, is called a *macroscopic* state.

(8) **Outline of the Statistical Mechanical Method**: If it is desired to calculate some property of a system which can be observed experimentally, the best that can be done is to obtain an average value taken over a large number of systems. It will be shown that by far the largest number of systems have one value of this property, the most probable value. It is this value, instead of the average, that is generally sought. This value will be that of the most probable "macroscopic" state, or, in other words, of the most probable distribution of coordinates and momenta. If we find this distribution for the most probable state, the property we seek can be calculated from it.

To study the most probable distribution we might take a large number of systems each consisting of the same number of molecules, each system in the same shaped container and with the same total energy but without any other restriction on the coordinates and momenta. Such a collection of systems is called an *assembly*. After a sufficiently long time the number of systems in any given configuration would approach a constant quantity. That is, as each system changed to a new configuration, another would assume the old configuration and a third would vacate the configuration to which the system changed. In terms of the γ-space for the system of molecules, the number of systems in any volume element dv_γ would be constant.

Our problem is to find the number of systems in each volume element in the γ-space when this state—the state of statistical equilibrium—is reached. To say that we know the number of systems in each volume element of the γ-space is to say that we know the microscopic state of each system of the assembly. Many microscopic states correspond to any macroscopic state. We find what *macroscopic* state has the largest number of systems in the assembly in micro-

scopic states corresponding to it. This is our most probable macroscopic state and the number of molecules for each of the corresponding systems in each of the various cells of the μ-space gives us our most probable distribution.

To find the condition of the assembly at statistical equilibrium (i.e., the distribution of systems in the γ-space) we must apply the general laws of mechanics to the systems of the assembly. Inasmuch as this is the only application of mechanics in the entire method a brief outline of the treatment will be given. It is required to find how the distribution of the points for the assembly in the γ-space changes with time and what sort of a distribution will not change with time. This information is contained in Liouville's Theorem.

(9) **Liouville's Theorem:** Suppose that ρ represents the density in the γ-space of the points representing the configurations of systems in the assembly, at the point $q_1{}^1, \cdots, q_r{}^n, p_1{}^1, \cdots, p_r{}^n$. The number of points in an element of "volume" is

$$\delta N = \rho \delta q_1{}^1 \cdots \delta q_r{}^n \delta p_1{}^1 \cdots \delta p_r{}^n.$$

Consider two "faces" of the elementary "volume" perpendicular to the axis of $q_1{}^1$. The number of points entering the volume element per second through this face is

$$\rho \dot{q}_1{}^1 \delta q_2{}^1 \cdots \delta q_r{}^n \delta p_1{}^1 \delta p_2{}^1 \cdots \delta p_r{}^n,$$

where, as is customary, the dot above the q represents the time derivative. The number leaving through the opposite face is

$$\left(\rho + \frac{\partial \rho}{\partial q_1{}^1} \delta q_1{}^1 \right) \left(\dot{q}_1{}^1 + \frac{\partial \dot{q}_1{}^1}{\partial q_1{}^1} \delta q_1{}^1 \right) \delta q_2{}^1 \cdots \delta q_r{}^n \delta p_1{}^1 \cdots \delta p_r{}^n.$$

The net number entering the volume element per second through these faces is obtained by subtracting the second from the first expression. The total rate of change of δN with time is given by summing the resulting expression over all coordinates and momenta, thus,

$$\frac{d(\delta N)}{dt} = - \sum_{\alpha=1}^{\alpha=n} \sum_{i=1}^{i=r} \left[\rho \left(\frac{\partial \dot{q}_i{}^\alpha}{\partial q_i{}^\alpha} + \frac{\partial \dot{p}_i{}^\alpha}{\partial p_i{}^\alpha} \right) + \left(\frac{\partial \rho}{\partial q_i{}^\alpha} \dot{q}_i{}^\alpha + \frac{\partial \rho}{\partial p_i{}^\alpha} \dot{p}_i{}^\alpha \right) \right]$$
$$\delta q_1{}^1 \cdots \delta q_r{}^n \delta p_1{}^1 \cdots \delta p_r{}^n, \quad (9.1)$$

where higher order differentials have been neglected.

It is at this point that the laws of mechanics are used. They are conveniently introduced in the form of the canonical equations of motion,

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \quad \text{and} \quad \dot{p}_i = - \frac{\partial H}{\partial q_i}. \quad (9.2)$$

Substituting these equations in (9.1) and noting that the order of partial differentiation is immaterial, the first term of the second member is zero and hence,

after division by the volume element $\delta v = \delta q_1{}^1 \cdots \delta p_r{}^n$,

$$\left(\frac{\partial \rho}{\partial t} \right)_{q,p} = - \sum_{\alpha=1}^{\alpha=n} \sum_{i=1}^{i=r} \left(\frac{\partial \rho}{\partial q_i{}^\alpha} \dot{q}_i{}^\alpha + \frac{\partial \rho}{\partial p_i{}^\alpha} \dot{p}_i{}^\alpha \right). \qquad (9.3)$$

This is *Liouville's Theorem.* It states that at any *fixed position* in the γ-space the rate of change of density which would occur with the time is equal and opposite to the change in density per second in the neighborhood of a point, moving according to mechanical laws, as it passes through the γ-space, if the rest of the assembly were stationary with respect to time; i.e.,

$$\frac{d\rho}{dt} = 0. \qquad (9.4)$$

As a point moves through the γ-space, therefore, the total change in density in its neighborhood is zero: this principle is known as that of *the conservation of density in phase.*

Suppose the systems are distributed initially as some function of their energy; the terms $\partial \rho / \partial q_i{}^\alpha$, $\partial \rho / \partial p_i{}^\alpha$ are then zero as ρ is a function of neither the q's nor the p's; then

$$\left(\frac{\partial \rho}{\partial t} \right)_{q,p} = 0 \qquad (9.5)$$

and the density of the points in the γ-space in any fixed locality does not change with the time.

If we consider once more the significance of the distribution of the points in the γ-space, the importance of this fact can readily be seen. Any point in the γ-space represents the exact configuration of a system containing n molecules; that is, its location in a given cell in the γ-space specifies the number of molecules in each cell in the μ-space or the distribution in the system. Equation (9.5) says, then, that the number of systems with any given distribution does not change with time. The macroscopic configuration, with the largest number of points in the γ-space corresponding to it, is that corresponding to the most probable distribution. This most probable distribution does not change with time and so *the assembly is in statistical equilibrium.*

A special case of the distribution of points in the γ-space as a function of their energy is that in which all the systems have energies within the range E and $E + dE$. Over this range the density is taken as a constant, and the assembly is in statistical equilibrium. It is of course obvious in this case that by definition $\partial \rho / \partial q_i{}^\alpha = 0$ and $\partial \rho / \partial p_i{}^\alpha = 0$ and hence that $(\partial \rho / \partial t)_{q,p} = 0$. It is this latter type of assembly, known as the *microcanonical assembly*, with which we shall deal.

Thus we shall assume that there is an equal chance of a system having any of the microscopic configurations that are consistent with the total energy E. For example, consider n weakly interacting molecules of a monatomic gas in a container. By weakly interacting is meant that any forces of attraction

(or repulsion) acting at a distance are so small that they may be neglected. We assume that there is just as much chance of *any one* of the configurations in which a single molecule has a velocity giving it the entire kinetic energy of the container in the x-direction and zero velocity in the y- and z-directions with zero velocity for the rest of the molecules, as there is of the configuration with the energy distributed equally among all molecules in all directions (providing the accuracy of the specification is the same in each case).

(10) **The Derivation of the Distribution Law:** There are n ways of giving a single molecule the entire kinetic energy of the system but there is only one way of distributing the kinetic energy so that each molecule has the same kinetic energy equally distributed in the x-, y- and z-directions. There are $n(n-1)$ ways of giving one molecule half the kinetic energy of the container in the x-direction and another the other half in the y-direction but only $n(n-1)/2$ ways of giving two molecules each half the kinetic energy in the x-direction. This is because the $n(n-1)$ ways include all cases where a pair of molecules with an identical configuration is exchanged which does not give a new point in the γ-space. There are always two molecules in the cell in the γ-space with $\dot{x} = p_x/m = (2E)^{1/2}$. Interchanging the members of this pair does not give rise to a new microscopic state. The distribution of energy, with the maximum distinguishable number of ways of attaining that distribution, is the most probable distribution. Each distinguishable way is a microscopic state corresponding to the macroscopic state of the distribution. This is as far as we can conveniently be specific in the matter. Let us suppose that there are n identical molecules of any type each with r degrees of freedom. Consider a macroscopic state defined as follows:

> Let there be n_1 molecules in the first cell of the r dimensional μ-space; that is, n_1 molecules whose coordinates and momenta lie within a given range between $(q_1, q_2, \cdots, q_r, p_1, p_2, \cdots, p_r)_1$ and $(q_1 + dq_1, q_2 + dq_2, \cdots, q_r + dq_r, p_1 + dp_1, p_2 + dp_2, \cdots, p_r + dp_r)_1$. Let there be n_2 molecules in the second cell; that is, n_2 molecules whose coordinates lie in some other range $(q_1, q_2, \cdots, q_r, p_1, p_2, \cdots, p_r)_2$ and $(q_1 + dq_1, q_2 + dq_2, \cdots, q_r + dq_r, p_1 + dp_1, p_2 + dp_2, p_r + dp_r)_2$. In general, n_i represents the number of molecules in the ith cell, there being η cells in all. The volumes of the cells, $dq_1 dq_2 \cdots dq_r \, dp_1 dp_2 \cdots dp_r$, are all the same.

Exchanging molecules between cells does not produce any change in the properties of the system but each exchange made *does* make the point for the system change to another cell in the γ-space and hence represents a new macroscopic state. How many different microscopic states are possible, without changing the number of molecules in the η cells of the μ-space, which would produce another macroscopic state with different physical properties?

There are $n!$ ways of arranging all n molecules but this number includes arrangements which differ only in arrangement of molecules *within* single cells in the μ-space. Rearrangement of molecules *within* cells of the μ-space does

not give rise to a new microscopic state and is therefore not to be counted. There are $n_1!$ ways of arranging the molecules in the first cell, $n_2!$ for those in the second and in general $n_i!$ for those in the ith cell. Thus the number of microscopic states is

$$P = \frac{n!}{n_1!\, n_2!\, n_3!\, \cdots\, n_i!\, \cdots\, n_\eta!}, \tag{10.1}$$

the product in the denominator being taken over all cells. The most probable distribution is that with values of n_1, n_2, n_3 etc., which make P a maximum. The condition that P be a maximum is that $\delta P = 0$, and therefore that $\delta \ln P = 0$.

$$\delta \ln n! - (\delta \ln n_1! + \delta \ln n_2! \cdots + \delta \ln n_i! + \cdots) = 0. \tag{10.2}$$

According to Stirling's approximation formula for the factorial, if the n's are large,

$$\ln n! = n \ln n - n, \tag{10.3}$$

if second order terms are neglected. Introducing this relation into (10.2) and remembering that n is a constant and therefore $\delta \ln n! = 0$

$$\ln n_1 \delta n_1 + \ln n_2 \delta n_2 + \cdots + \ln n_i \delta n_i + \cdots + \ln n_\eta \delta n_\eta \cdots = 0. \tag{10.4}$$

If the change $\delta \ln P$ is made by arbitrary changes δn_1, δn_2, $\cdots$, δn_i, $\cdots$, in all the n_i's, the only solution to equation (10.4) would be that $\ln n_1 = \ln n_2 = \cdots = \ln n_i = 0$ or that all the n_i are equal, meaning equal distribution among μ-space cells. Actually all of the δn_i's are not arbitrary as they are subject to the conditions that

$$n_1 + n_2 + \cdots + n_i + \cdots + n_\eta = n \tag{10.5}$$

and

$$\epsilon_1 n_1 + \epsilon_2 n_2 + \cdots + \epsilon_i n_i + \cdots + \epsilon_\eta n_\eta = E, \tag{10.6}$$

where ϵ_i is the energy increase in the system when a molecule is introduced into the ith cell. Equation (10.5) says that the total number of molecules is constant and equation (10.6) that the total energy is constant; thus

$$\delta n_1 + \delta n_2 + \cdots + \delta n_i + \cdots + \delta n_\eta = 0 \tag{10.7}$$

and

$$\epsilon_1 \delta n_1 + \epsilon_2 \delta n_2 + \cdots + \epsilon_i \delta n_i + \cdots + \epsilon_\eta \delta n_\eta = 0. \tag{10.8}$$

These two relations (10.7) and (10.8) limit the arbitrariness of the δn_i. They may be looked on as showing how δn_1 and δn_2 depend on the remaining $\eta - 2$ quantities δn_i. Multiplying (10.7) by α and (10.8) by β and adding both to (10.4) gives

$$\sum_{i=1}^{i=\eta} (\ln n_i + \alpha + \beta \epsilon_i) \delta n_i = 0. \tag{10.9}$$

By choosing α and β to make

$$(\ln n_1 + \alpha + \beta\epsilon_1) = 0 \quad \text{and} \quad (\ln n_2 + \alpha + \beta\epsilon_2) = 0, \qquad (10.10)$$

we thus eliminate the first two terms in the sum on the left-hand side of (10.9) which are the only terms with δn_1 and δn_2; then

$$\sum_{i=3}^{i=\eta} (\ln n_i + \alpha + \beta\epsilon_i)\delta n_i = 0. \qquad (10.11)$$

Equation (10.11) now only contains δn_3, δn_4, $\cdots$, δn_η, which are independent as a result of the artifice; hence, the only solution of (10.11) is that all $\eta - 2$ quantities are zero, i.e.,

$$\ln n_i + \alpha + \beta\epsilon_i = 0, \qquad (10.12)$$

which is true for all the n_i, as this quantity for n_1 and n_2 was made zero by adjustment of α and β. Equation (10.12) becomes

$$n_i = e^{-(\alpha + \beta\epsilon_i)} \qquad (10.13)$$

or

$$n_i = C''e^{-\beta\epsilon_i}, \qquad (10.14)$$

where $C'' = e^{-\alpha}$ is a new constant. Equation (10.14) is the *Maxwell-Boltzmann distribution law.*

(11) **Other Forms of the Maxwell-Boltzmann Distribution Law**: Equation (10.14) takes on a simple form if we consider only the translational degrees of freedom and consider these to be classically excited. The number of molecules in the ith cell of the μ-space depends on the size initially (and arbitrarily) chosen for all the cells in the μ-space, viz., $dq_1dq_2 \cdots dq_r\, dp_1dp_2 \cdots dp_r$. Thus, writing dn for n_i and dropping the subscript on ϵ,

$$dn = C'e^{-\beta\epsilon}dq_1dq_2 \cdots dq_rdp_1dp_2 \cdots dp_r. \qquad (11.1)$$

In any practical case

$$\epsilon = \tfrac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + f(x, y, z, q_4, \cdots, q_r, p_4, \cdots, p_r),$$

where x, y and z are now written for q_1, q_2 and q_3 and $m\dot{x}$, $m\dot{y}$ and $m\dot{z}$ for p_1, p_2 and p_3 respectively. Then equation (11.1) becomes

$$dn = C'm^3e^{-\beta f(x,\,y,\,z,\,q_4,\,\cdots,\,q_r,\,p_4,\,\cdots,\,p_r)}dxdydzdq_4 \cdots dq_rdp_4 \cdots dp_r$$
$$e^{-\beta m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)/2}d\dot{x}d\dot{y}d\dot{z}. \qquad (11.2)$$

Integrating over all variables except $\dot{x}$, $\dot{y}$ and $\dot{z}$ we have

$$dn = Be^{-\beta m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)/2}d\dot{x}d\dot{y}d\dot{z}, \qquad (11.3)$$

where B stands for the constant factors obtained by integration combined

with C' and m^3. This equation gives the number of molecules with components of velocity $\dot{x}$, $\dot{y}$ and $\dot{z}$ lying in the range $d\dot{x}d\dot{y}d\dot{z}$. The resultant translational velocity c, of a molecule is given by

$$c^2 = \dot{x}^2 + \dot{y}^2 + \dot{z}^2, \tag{11.4}$$

$$\begin{aligned} \dot{x} &= c \sin\theta \cos\phi \\ \dot{y} &= c \sin\theta \sin\phi \\ \dot{z} &= c \cos\theta, \end{aligned} \tag{11.5}$$

where θ is the angle made by the direction of c with the $\dot{z}$ (or z) axis and ϕ the angle made by the projection of c on the xy plane with the $\dot{x}$ (or x) axis. Thus c, θ and ϕ are the polar coordinates corresponding to $\dot{x}$, $\dot{y}$ and $\dot{z}$. Transforming (11.3) accordingly

$$dn = Bc^2 \sin\theta e^{-\beta mc^2/2} dcd\theta d\phi \tag{11.6}$$

gives the number of molecules having a speed c, and a direction of motion given by the angles θ and ϕ in the range $d\theta d\phi dc$. Integration of (11.6) with respect to θ and ϕ yields

$$dn = Ac^2 e^{-\beta mc^2/2} dc \tag{11.7}$$

for the number of molecules of speed between c and $c + dc$, without regard to direction, where A is a new constant. Equation (11.7) is Maxwell's distribution law of velocities. By using it the value of β can readily be obtained.

(12) **The Evaluation of the Constants related to α:** The constant C' in equation (11.1) is readily evaluated by noting that the integration of this expression yields the total number of molecules.

$$n = \int dn = C' \int \cdots \int e^{-\beta \epsilon} dq_1 \cdots dp_r. \tag{12.1}$$

Thus

$$C' = \frac{n}{\displaystyle\int \cdots \int e^{-\beta \epsilon} dq_1 \cdots dp_r}, \tag{12.2}$$

where the integration is carried out over the range of the p's ($-\infty$ to $+\infty$) and of the q's.

Similarly for B in equation (11.3) one obtains

$$B = \frac{n}{\displaystyle\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} e^{-\beta m(\dot{x}^2+\dot{y}^2+\dot{z}^2)/2}} d\dot{x}d\dot{y}d\dot{z} \tag{12.3}$$

or

$$B = \frac{n}{\left(\displaystyle\int_{-\infty}^{+\infty} e^{-\beta m\dot{x}^2/2} d\dot{x}\right)\left(\displaystyle\int_{-\infty}^{+\infty} e^{-\beta m\dot{y}^2/2} d\dot{y}\right)\left(\displaystyle\int_{-\infty}^{+\infty} e^{-\beta m\dot{z}^2/2} d\dot{z}\right)}, \tag{12.4}$$

since x, y and z are independent. Moreover, the three integrals are obviously numerically equal. They are equivalent to $\int_{-\infty}^{+\infty} e^{-ax^2}dx = (\pi/a)^{1/2}$. Thus

$$B = \frac{n}{\left(\dfrac{2\pi}{\beta m}\right)^{3/2}} = n\left(\frac{\beta m}{2\pi}\right)^{3/2}. \tag{12.5}$$

Similarly we deduce that A in equation (11.7) is given by

$$A = 4\pi n \left(\frac{\beta m}{2\pi}\right)^{3/2}. \tag{12.6}$$

(13) **The Evaluation of the Constant** β: It is not difficult to set up a relation like equation (11.1) for the case where several different kinds of weakly interacting molecules are present in the container. The distribution law is then obtained which gives an equation like equation (11.14) for each type of molecule, each with a different α but all with the same β (number of *each kind* constant, *total* energy constant).

To evaluate β, consider a system part of which consists of a cubical vessel with sides of length l, parallel to the coordinate axes, containing n molecules of a monatomic gas: the pressure of the gas is then calculated in terms of the parameter β. Consider an area dS on the wall; any molecule suffers a change of momentum of $2m\dot{x}$ on striking the wall. There are $\rho_{\dot{x}}\dot{x}dS$ collisions with the wall per second, where $\rho_{\dot{x}}$, the density of molecules having $\dot{x}$ as their x-component of velocity is defined by

$$\rho_{\dot{x}} = B\frac{\displaystyle\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} e^{-\beta m(\dot{x}^2+\dot{y}^2+\dot{z}^2)/2}d\dot{x}d\dot{y}d\dot{z}}{l^3}. \tag{13.1}$$

The rate of change of momentum per second over the area dS is given by $2m\rho_{\dot{x}}\dot{x}^2dS$: this is the force acting on the area dS due to molecules with the velocity $\dot{x}$, and the total force is obtained by integrating over all values of $\dot{x}$. The total force, however, is PdS, so that after substituting for $\rho_{\dot{x}}$ we have

$$PdS = \frac{2mdSB}{l^3}\int_{0}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \dot{x}^2 e^{-\beta m(\dot{x}^2+\dot{y}^2+\dot{z}^2)/2}d\dot{x}d\dot{y}d\dot{z}. \tag{13.2}$$

The evaluation of the triple integral in (13.2) is made readily by using

$$\int_{0}^{\infty} e^{-ax^2}dx = \tfrac{1}{2}\left(\frac{\pi}{a}\right)^{1/2} \quad \text{and} \quad \int_{0}^{\infty} e^{-ax^2}x^2dx = \tfrac{1}{4}\left(\frac{\pi}{a^3}\right)^{1/2}.$$

Thus

$$P = \frac{2mB}{l^3}\cdot\frac{1}{2\beta m}\left(\frac{2\pi}{\beta m}\right)^{3/2}, \tag{13.3}$$

after cancelling dS from both sides. Since $l^3 = V$, the volume of the container, it is only necessary to substitute for B from equation (12.5), whence

$$P = \frac{n}{V\beta} \qquad \text{or} \qquad PV = \frac{n}{\beta}. \qquad (13.4)$$

Since $PV = nkT$, it follows that

$$\beta = 1/kT. \qquad (13.5)$$

(14) The Final Form of the Classical Maxwell-Boltzmann Distribution Law: Substituting for the constants in equation (11.1) from equations (12.2) and (13.5) we obtain

$$dn = \frac{ne^{-\epsilon/kT}dq_1 \cdots dq_r\, dp_1 \cdots dp_r}{\int \cdots \int e^{-\epsilon/kT}dq_1 \cdots dq_r\, dp_1 \cdots dp_r}, \qquad (14.1)$$

which gives the number of molecules with coordinates and momenta in a given range for a completely classical system. A minor modification of this is applicable to most quantum systems as will be shown later. The same considerations that were used in obtaining equation (11.3) can be used to show that the relations

$$dn = \frac{ne^{-\epsilon_q/kT}dq}{\int e^{-\epsilon_q/kT}dq} \qquad \text{or} \qquad dn = \frac{ne^{-\epsilon_p/kT}dp}{\int e^{-\epsilon_p/kT}dp} \qquad (14.2)$$

give the number of molecules with a particular coordinate or a particular momentum in a given range, where ϵ_q is the part of the energy due to q and ϵ_p that due to p. This relation is only true if the expression for the total energy of a molecule depends on q or p through terms not containing the other variables, i.e., when $\epsilon_{total} = \epsilon_q + $ a function of the other variables or when $\epsilon_{total} = \epsilon_p + $ a function of the other variables. Similarly, expression (14.1) can be applied to a chosen number of the p's and q's whenever the energy depends on these p's and q's only through terms not containing the other variables.

(15) The Several Forms of the Maxwell Distribution: By substituting equations (12.5) and (13.5) in equation (11.3) one obtains

$$dn = n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-m(\dot{x}^2+\dot{y}^2+\dot{z}^2)/2kT}d\dot{x}d\dot{y}d\dot{z} \qquad (15.1)$$

for the number of molecules having components of velocity $\dot{x}$, $\dot{y}$ and $\dot{z}$ in the range $d\dot{x}d\dot{y}d\dot{z}$. Equation (15.1) in polar coordinates is

$$dn = n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mc^2/2kT}c^2 \sin\theta dc d\theta d\phi. \qquad (15.2)$$

By substituting equations (12.6) and (13.5) in equation (11.7) there is obtained

$$dn = 4\pi n \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-mc^2/2kT} c^2 dc \tag{15.3}$$

for the number of molecules with speed between c and $c + dc$ irrespective of direction.   Substituting ϵ for the kinetic energy $\frac{1}{2}mc^2$ in equation (15.3) the result is

$$dn = 2\pi n \left(\frac{1}{\pi kT} \right)^{3/2} e^{-\epsilon/kT} \epsilon^{1/2} d\epsilon \tag{15.4}$$

for the number of molecules whose kinetic energy lies between ϵ and $\epsilon + d\epsilon$.

(16) **Averages in Statistical Mechanics:** Consider a property G whose value depends on all the coordinates and momenta of the system.   The average value of this G is obtained by multiplying each value of the property G by the number of molecules which have it, summing (integrating) over all the molecules in the system, and finally dividing by the total number of molecules in the system.   Denoting this average by $\bar{G}$ we have,

$$\bar{G} = \frac{\int \cdots \int G e^{-\epsilon/kT} dq_1 \cdots dq_r \, dp_1 \cdots dp_r}{\int \cdots \int e^{-\epsilon/kT} dq_1 \cdots dq_r \, dp_1 \cdots dp_r} . \tag{16.1}$$

(17) **The Principle of Equipartition of Energy:** When the energy is proportional to the square of a given coordinate or momentum, it can be shown that the average energy due to that coordinate or momentum is simply $kT/2$ per molecule.   Suppose

$$\epsilon = \frac{p_i^2}{2m} + \phi, \tag{17.1}$$

where ϕ is a function of the rest of the p's and q's.   We wish to compute $\bar{\epsilon}_{p_i}$ the average value of $p_i^2/2m$.   According to (16.1) this is given by,

$$\bar{\epsilon}_{p_i} = \frac{\int \cdots \int \frac{p_i^2}{2m} e^{-p_i^2/2mkT} e^{-\phi/kT} dq_1 \cdots dq_r \, dp_1 \cdots dp_i \cdots dp_r}{\int \cdots \int e^{-p_i^2/2mkT} e^{-\phi/kT} dq_1 \cdots dq_r \, dp_1 \cdots dp_i \cdots dp_r} . \tag{17.2}$$

Since the first two factors in the integrand of the numerator and the first in the denominator depend on p_i alone, the rest of the variables can be integrated out in both numerator and denominator without affecting these factors.   It is obvious that the result yields factors all of which cancel from the numerator

and denominator so that

$$\bar{\epsilon}_{p_i} = \frac{\int_{-\infty}^{\infty} \frac{p_i^2}{2m} e^{-p_i^2/2mkT} dp_i}{\int_{-\infty}^{\infty} e^{-p_i^2/2mkT} dp_i}$$

$$= \frac{1}{2m} \cdot \frac{\frac{1}{2}\sqrt{\pi(2mkT)^3}}{\sqrt{\pi(2mkT)}}$$

$$= kT/2. \tag{17.3}$$

(18) **Energy and Heat Capacity in Classically Excited Systems:** The result in equation (17.3) can be applied at once to calculate the translational energy and heat capacity (at constant volume) of a gas, which, in the case of a monatomic gas, is, the total energy and heat capacity. There are three translational degrees of freedom. The kinetic energy depends on the squares of the momenta associated with each of the coordinates. Thus the total translational energy is $3kT/2$ per molecule or $3RT/2$ per mole. The heat capacity at constant volume is the derivative of this quantity with respect to temperature, i.e., $3R/2$ calories per degree per mole. For the energy and heat capacity at constant volume due to translation and external rotation of a polyatomic gas, there are three more degrees of freedom upon which the kinetic energy depends through the square of the associated momenta. The energy and heat capacity at constant volume are $3RT$ and $3R$ respectively for the translational and rotational degrees of freedom. For a diatomic gas the corresponding quantities are $5RT/2$ and $5R/2$.

The energy of a solid is mostly stored in vibrational degrees of freedom and the same is true for the internal energy of a polyatomic molecule. For each such degree of freedom the energy depends on the square of the coordinate and of the associated momentum. Thus the energy will be RT per degree of freedom for each mole if the vibration is classically excited.

(19) **Statistical Mechanics Applied to Quantized Systems—General:** Consider a system of N particles (electrons, atoms or molecules) * which constitute a single phase (gas, liquid or crystal). Let the zeroth order wave functions of a particle be ϕ_1, ϕ_2, etc. A zeroth order wave function for the system is

$$\psi_1 = \phi_1(1)\phi_2(2)\phi_3(3) \cdots \phi_N(N), \tag{19.1}$$

where $\phi_i(k)$ means that the kth particle is in a quantum state characterized by the wave function ϕ_i.

The wave function ψ_1 satisfies the zeroth order wave equation for the system. Other such wave functions can be obtained by permuting the wave

---

* In general, throughout this discussion, the word particle is used as a general term. A particle may be an electron, a nucleus, an atom, or a molecule without distinction, unless otherwise stated.

functions ϕ_i among the particles; thus

$$\psi_2 = \phi_1(2)\phi_2(1)\phi_3(3) \cdots \phi_N(N) \qquad (19.2)$$

represents another solution. All the wave functions ψ_i correspond to the same energy. Any linear combination of the wave functions, ψ_i, will satisfy the zeroth order wave equation for the system. The allowed solutions of the zeroth order wave function for the system are either the linear combination with all the coefficients $+1$, or the one with coefficients $+1$ for terms produced by even permutation of particles and -1 for terms produced by odd permutation. The former does not change sign when particles are permuted in the entire linear combination while the latter does change its sign. The former is called the *symmetric* wave function and is possessed by systems of particles composed of an even number of elementary particles (protons, neutrons, and electrons) while the latter is called the *antisymmetric* wave function and is possessed by particles composed of an odd number of elementary particles. In the latter case none of the functions ϕ_i can be identical.

When the correct wave functions and energies are obtained by a perturbation method, it may happen that the correct wave functions closely resemble the wave functions ψ_i. If high energy barriers prevent rearrangement of the particles in space corresponding to a change of the system from ψ_i to ψ_j, the particles are then identifiable with their permanent locations (wave functions). Such systems are called systems of *localized elements*. Crystalline substances are in this class.

It is quite evident therefore that, except in systems of localized elements, it is meaningless to consider particles as identifiable. If the particles are not identifiable, equation (10.1) no longer gives the correct number of microscopic states since in deriving it new microscopic states were obtained by exchange of particles. Such an exchange does not give rise to a new microscopic state when the particles cannot be identified. Thus, in general, equation (10.1) cannot be applied to translation.

Presently we shall derive the correct expressions for the number of microscopic states corresponding to symmetric and antisymmetric wave functions and from them deduce the distribution laws. It will be shown that, for atoms and molecules in gases, under practical conditions the distribution laws for translational motion reduce to the Maxwell-Boltzmann distribution law (10.14). This is not the case for electrons.

In crystals the elements are localized. In this case the wave functions ϕ are the vibrational wave functions of the particles. Each one of these can be considered as any of the vibrational eigenfunctions but applying to a definite position in the crystal. Interchange of different vibrational eigenfunctions between positions produces a new microscopic state but exchanging particles merely between positions does not. Under any circumstances the degrees of freedom other than translation are localized because the particles are identifiable with their positions in space or their translational momenta. In this case the

wave functions, ϕ, are the product of the rotational, vibrational and bound electronic wave functions. For these systems (10.1) is correct.

In the application of statistical mechanics to quantized systems, it is necessary to assign to each quantum state, for a particular degree of freedom, the area lying between two paths in a coordinate space with p plotted against the corresponding q. To the state of lowest energy we assign the area included by the corresponding path To the next state we assign the area between this path and the next and so on. Thus corresponding to the specification of the degree of freedom for a particle as lying in a particular range $dqdp$, we say that the energy due to this degree of freedom has a certain value and that the configuration and momenta are within the range $dqdp = h$. Thus it is seen that in a system of molecules, each with r degrees of freedom, a volume in the μ-space of h^r will be assigned to a quantum state defined by a set of r quantum numbers. It will be convenient to take this as our new unit of volume and to let each cell in the μ-space be of unit volume.

(20) **The Distribution Law for Systems of Localized Elements:** In the case of rotational, vibrational and bound electronic degrees of freedom, including those of a crystal, equation (10.1) holds for the number of microscopic states. In this expression let n_1, n_2, $\cdots$, n_j denote the number of molecules in each quantum state (i.e., in each of the unit cells of the μ-space).

Evidently the distribution law for the most probable state of the system is

$$n_j = e^{-(\alpha+\beta\epsilon_j)} = Ce^{-\beta\epsilon_j}, \tag{20.1}$$

which is deduced by following exactly the same procedure that was used in deriving (10.13). The subscript j is taken to denote the entire set of quantum numbers characterizing the state of the molecule. In the case of a crystal composed of atoms, the normal coordinates replace the Cartesian coordinates. Each mode can be thought of as a linear oscillator and thus n_j gives the number of modes with a particular value of the single quantum number involved (i.e., in a single cell in a one dimensional μ-space).

Sometimes certain quantum numbers of the set affect the motion but not the energy. States of a molecule which differ only in these quantum numbers (degenerate states) are usually grouped together. The number of molecules in such a group is

$$n_i = p_i e^{-(\alpha+\beta\epsilon_i)} = Cp_i e^{-\beta\epsilon_i}, \tag{20.2}$$

where i stands only for those quantum numbers which determine the energy, and p_i, the number of states * with the same energy, is known as the *a priori probability* or *statistical weight of the group*.

At high temperatures, the laws of quantum mechanics approach those of classical mechanics. This is due to the fact that, for large quantum numbers, the energy difference between states is small compared with the total energy.

---

* The symbol p is also used for the momentum; in view of the different nature of the two quantities, no confusion is likely.

Under these circumstances, several quantum states can be grouped together and taken as having essentially the same energy. Let the volume in the μ-space corresponding to the group of states be $dq_1 \cdots dq_r \, dp_1 \cdots dp_r/h^r$ in the new units. The number of states in the group is equal to this volume. The number of molecules in this group, according to equation (20.2), is

$$dn = Ce^{-\beta\epsilon}dq_1 \cdots dq_r \, dp_1 \cdots dp_r/h^r. \tag{20.3}$$

Equation (20.3) is the distribution law in the classical limit for systems of localized elements; it is identical with equation (11.1), and since it was proved that $\beta = 1/kT$ for that equation, it follows that $\beta = 1/kT$ in (20.1), (20.2) and (20.3).

The constant C in equation (20.1) and (20.2) can be obtained by summing n_i over all groups of quantum states. The sum is equal to the total number of molecules, n; thus,

$$C = \frac{n}{\sum\limits_{i} p_i e^{-\epsilon_i/kT}} \cdot \tag{20.4}$$

The distribution law for the number of molecules in the different quantum states of a system of localized particles is

$$n_j = \frac{ne^{-\epsilon_j/kT}}{\sum\limits_{i} p_i e^{-\epsilon_i/kT}}, \tag{20.5}$$

where i stands only for the set of quantum numbers which determines the energy, but j stands for the entire set. The number of molecules in a group of quantum states with the same energy (degenerate states) is

$$n_i = \frac{np_i e^{-\epsilon_i/kT}}{\sum p_i e^{-\epsilon_i/kT}} \cdot \tag{20.6}$$

(21) The Partition Function: The sum in the denominator of equation (20.4) is called the *partition function*, denoted by Q. The term partition function is due to Fowler; this quantity was first called the *zustandssumme* by Planck and has been translated *sum-over-states* by Tolman. It enters into the calculation of all thermodynamic quantities from statistical mechanics. For all systems, obeying the Boltzmann distribution law, the partition function is defined as

$$Q = \sum\limits_{i} p_i e^{-\epsilon_i/kT} = n/C. \tag{21.1}$$

(22) The Einstein-Bose Distribution Law: We shall now derive the distribution law which is applicable to a system of particles which has symmetric wave functions; this is a characteristic of most neutral molecules. It is necessary to find the number of microscopic states which correspond to conditions

first of definite energy and second of definite pressure for the system (a macroscopic state). The second requirement is fulfilled by fixing the number of molecules as n in a container of volume V, and the first requirement is fulfilled by a limitation on the choice of the wave functions for the particles to be distributed among the n nonidentified particles. Let ϵ_k be the energy of a group of p_k degenerate wave functions whose members may or may not be characterized by the same quantum numbers. Let there be n_k particles with quantum states in this group and therefore with the energy ϵ_k. The total energy of the system is given by

$$E = \sum_k n_k \epsilon_k = \text{const.} \tag{22.1}$$

The energy has been equated to a constant to satisfy the first requirement while the second requirement demands that

$$\sum n_k = n. \tag{22.2}$$

We have now to find a general expression for the number of microscopic states, P, corresponding to n_1 particles in the first group of p_1 states with energy ϵ_1, n_2 in the second group of p_2 states with energy ϵ_2, etc., and n_k in the kth group of p_k states of energy ϵ_k, etc. This expression is to be used to find $n_1, n_2, \cdots, n_k, \cdots$ for the most probable state of the system, i.e. in the case when the number of microscopic states is a maximum. To obtain this expression we can find the number of ways (O_k) of distributing the n_k *indistinguishable* particles among the p_k states for each group and take the products of the numbers thus obtained for all groups ($\Pi_k O_k$). Let us take ($p_k - 1$) partitions to separate the particles into p_k regions, each region representing a state. For example, one partition is required to divide the particles into two states, two partitions for division into three states, etc. The ($p_k - 1$) partitions mark off the same p_k regions in space after any permutation of the partitions. We have to find how many ways there are of distributing n_k identical particles among the p_k regions. The number of ways of permuting the ($n_k + p_k - 1$) objects made up of n_k particles and ($p_k - 1$) partitions is ($n_k + p_k - 1$)!. This number is many fold greater than the number O_k required. It is the product of the number of arrangements (O_k) of the indistinguishable particles among the regions, the number of ways of permuting the partitions, ($p_k - 1$)!, and the number of permutations, $n_k!$, of the particles among themselves which because of their indistinguishability is not to be included in O_k. Thus:

$$O_k = \frac{(n_k + p_k - 1)!}{n_k!(p_k - 1)!} \tag{22.3}$$

and

$$P = \Pi_k \frac{(n_k + p_k - 1)!}{n_k!(p_k - 1)!} \, . \tag{22.4}$$

Equation (22.4) now replaces (10.1) while (22.1) and (22.2) are identical with

(10.6) and (10.5). With this change we now proceed as we did to derive the Maxwell-Boltzmann distribution law. Using equation (10.3) and neglecting unity compared to $(n_k + p_k)$

$$\ln P = \sum_k \left[(n_k + p_k) \ln (n_k + p_k) - (n_k + p_k) - n_k \ln n_k \right.$$

$$\left. + n_k - p_k \ln p_k + p_k \right] \quad (22.5)$$

or

$$\ln P = \sum_k \left[n_k \ln \left(1 + \frac{p_k}{n_k} \right) + p_k \ln \left(1 + \frac{n_k}{p_k} \right) \right]. \quad (22.6)$$

The condition that the number of microscopic states be a maximum is

$$\delta \ln P = \delta \sum_k \left[n_k \ln \left(1 + \frac{p_k}{n_k} \right) + p_k \ln \left(1 + \frac{n_k}{p_k} \right) \right] = 0. \quad (22.7)$$

Remembering that p_k the number of states in a group is constant,

$$\sum_k \left[\ln \left(1 + \frac{p_k}{n_k} \right) \delta n_k + n_k \left(- \frac{p_k}{n_k^2} \right) \frac{n_k}{(n_k + p_k)} \delta n_k \right.$$

$$\left. + p_k \frac{1}{p_k} \cdot \frac{p_k}{(n_k + p_k)} \delta n_k \right] = 0, \quad (22.8)$$

$$\therefore \quad \sum_k \ln \left(\frac{p_k}{n_k} + 1 \right) \delta n_k = 0. \quad (22.9)$$

The variations δn_k are not all independent but are subject to the restrictions given by equations (22.1) and (22.2). In differential form these equations become

$$\sum_k \epsilon_k \delta n_k = 0 \quad (22.10)$$

and

$$\sum_k \delta n_k = 0. \quad (22.11)$$

These relations limit the complete arbitrariness of the δn_k so that two of them are dependent. Multiplying (22.10) by β and (22.11) by α and subtracting (22.9)

$$\sum_k \left[\beta \epsilon_k + \alpha - \ln \left(\frac{p_k}{n_k} + 1 \right) \right] \delta n_k = 0. \quad (22.12)$$

The constants β and α are chosen to make the quantity inside the square brackets zero for the first two terms in the sum $\sum\limits_k$, thus eliminating the two terms containing the dependent quantities δn_1 and δn_2. We then have the sum of two less terms in which the δn_k are all arbitrary equated to zero. Thus to satisfy the equality for arbitrary δn_k, the quantities in square brackets which

remain, must also be zero: i.e., in general,

$$\beta\epsilon_k + \alpha - \ln\left(\frac{p_k}{n_k} + 1\right) = 0, \qquad (22.13)$$

or

$$\frac{p_k}{n_k} + 1 = e^{(\beta\epsilon_k + \alpha)},$$

or

$$n_k = \frac{p_k}{e^{(\beta\epsilon_k + \alpha)} - 1} \cdot \qquad (22.14)$$

This is the *Einstein-Bose distribution law.*

(23) **The Fermi-Dirac Distribution Law:** To obtain the distribution law applicable to particles, such as electrons, with antisymmetrical wave functions we must remember that there can be only one particle with each wave function on account of the antisymmetrical character of the total wave function. Except for this restriction we proceed exactly as in the case of particles whose wave functions are symmetrical.

We must accordingly find the number of ways of assigning quantum states (wave functions), chosen from the group consisting of p_k states of energy ϵ_k, to the n_k indistinguishable particles in such a way that each state is assigned to only one particle: this can be done only when

$$p_k \gtreqless n_k. \qquad (23.1)$$

The number of ways, O_k, is simply the number of combinations of p_k states taken n_k at a time, i.e.,

$$O_k = p_k(p_k - 1)(p_k - 2) \cdots [p_k - (n_k - 1)]/n_k! = \frac{p_k!}{(p_k - n_k)!n_k!} \cdot \qquad (23.2)$$

The total number of microscopic states corresponding to the macroscopic state of the system is therefore

$$P = \prod_k \frac{p_k!}{(p_k - n_k)!n_k!} \cdot \qquad (23.3)$$

Equation (23.3) is subject to the conditions stated in equation (22.1) and (22.2); thus we must satisfy simultaneously

$$\delta \ln P = \sum_k \ln\left(\frac{p_k}{n_k} - 1\right)\delta n_k = 0, \qquad (23.4)$$

$$\sum_k \epsilon_k \delta n_k = 0, \qquad (23.5)$$

and

$$\sum_k \delta n_k = 0. \qquad (23.6)$$

By a method analogous to that used in the Einstein-Bose case, we obtain

$$n_k = \frac{p_k}{e^{\beta \epsilon_k + \alpha} + 1} \cdot \qquad (23.7)$$

This is the *Fermi-Dirac distribution law*.

(24) **Concerning the Evaluation of the Constant α:** If α is large or ϵ_k is large it can be seen at once that both (22.14) and (23.7) become

$$n_k = p_k e^{-\alpha} e^{-\beta \epsilon_k}, \qquad (24.1)$$

because the exponential term in the denominator will be large compared with unity. This is the Boltzmann distribution law with the constant equal to $e^{-\alpha}$. Thus we see that α plays the same role in (22.14) and (23.7) that it does in the Maxwell-Boltzmann distribution law and that its value is to be determined through

$$n = \sum_k \frac{p_k}{e^{\beta \epsilon_k + \alpha} \pm 1} \qquad (24.2)$$

with the plus sign applying to (23.7) and the minus sign to (22.14). Direct evaluation of α is difficult in either case because of the extra term in the denominator of (24.2). However, noting that the p_k are proportional to the volume of the container it follows that for any volume V of a particular system, α will be large whenever n is small, i.e., when the density is small.

(25) **The Value of the Constant β:** It is quite evident that β must have the same value for *all* systems including those where α is large or where large ϵ_k are involved. But in these latter cases both (22.14) and (23.7) become identical with the Maxwell-Boltzmann distribution law: thus

$$\beta = \frac{1}{kT} \qquad (25.1)$$

in the general case of all distribution laws.

(26) **Values of the Energy and Pressure of a Degenerate Gas Obeying the Einstein-Bose Distribution Law:** In this section we shall apply wave mechanical methods to a gas which consists of molecules or atoms containing an even number of elementary particles, and hence which has symmetrical wave functions. Such a gas obeys the Einstein-Bose distribution law. We do this in order to see under what conditions, if any, the properties (pressure and energy) of such a gas differ from those already deduced without regard to symmetry. We shall find, even at the lowest working temperatures, that the difference in properties is negligible.

Unit volume in the μ-space has been defined so that it corresponds to a single quantum state: hence the volume in the μ-space corresponding to the

energy range $d\epsilon$ can be placed equal to the number of states, p, i.e.,

$$p_s \int\int\int\int\int\int \frac{dxdydzdp_xdp_ydp_z}{h^3} = p. \tag{26.1}$$

The factor p_s, which is the number of spin quantum states of equal energy, has been introduced to allow for nuclear or electron spin which has not otherwise been counted. Equation (26.1) can be written

$$p_s \int\int\int\int\int\int \frac{m^3dxdydzd\dot{x}d\dot{y}d\dot{z}}{h^3} = p. \tag{26.2}$$

Integrating with respect to the coordinates which introduces the volume, V, as a factor and transforming $\dot{x}$, $\dot{y}$ and $\dot{z}$ to polar coordinates such that $\dot{x}^2 + \dot{y}^2 + \dot{z}^2 = c^2$

$$p_s \int\int\int \frac{m^3 V c^2 \sin\theta d\theta d\phi dc}{h^3} = p. \tag{26.3}$$

Since

$$\tfrac{1}{2}mc^2 = \epsilon, \tag{26.4}$$

$$c = \left(\frac{2\epsilon}{m}\right)^{1/2}, \tag{26.5}$$

and hence

$$dc = \frac{1}{2}\left(\frac{2\epsilon}{m}\right)^{-1/2}\frac{2}{m}d\epsilon = \left(\frac{1}{2m}\right)^{1/2}\epsilon^{-1/2}d\epsilon. \tag{26.6}$$

Substituting (26.4) and (26.6) in (26.3)

$$p = \frac{2^{1/2}m^{3/2}Vp_s}{h^3}\int\int\int \epsilon^{1/2}\sin\theta d\epsilon d\theta d\phi. \tag{26.7}$$

The limits of integration are as follows: for θ, 0 and π; for ϕ, 0 and 2π; for ϵ, ϵ and $\epsilon + d\epsilon$. The limits for ϵ mean that no integration with respect to ϵ is required: hence,

$$\frac{2^{1/2}m^{3/2}Vp_s}{h^3}\int_0^\pi\int_0^{2\pi} \epsilon^{1/2}\sin\theta d\epsilon d\theta d\phi = p, \tag{26.8}$$

$$\therefore \quad \frac{\pi 2^{5/2}m^{3/2}Vp_s}{h^3}\epsilon^{1/2}d\epsilon = p. \tag{26.9}$$

Substituting this result for p in equation (22.14),

$$dn = \frac{\pi 2^{5/2}m^{3/2}Vp_s}{h^3} \cdot \frac{\epsilon^{1/2}d\epsilon}{e^{(\epsilon/kT)+\alpha} - 1}, \tag{26.10}$$

which is the Einstein-Bose distribution law giving the number of molecules with

translational energy in the range between ϵ and $\epsilon + d\epsilon$ and with any of p_s spin states of equal energy.   It is to be noted that the nuclear or electron spin states thus counted must be excluded from calculations involving the internal or rotational degrees of freedom if the particles are molecules.[1]

Upon integration of (26.10) the result is

$$n = \frac{\pi 2^{5/2} m^{3/2} V p_s}{h^3} \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{e^{(\epsilon/kT)+\alpha} - 1},$$ (26.11)

and placing $\epsilon/kT = z$ and $(\tfrac{1}{2})\sqrt{\pi} = \Gamma(\tfrac{1}{2} + 1),$*

$$n = \frac{(2\pi m kT)^{3/2} V p_s}{h^3 \Gamma(\tfrac{1}{2} + 1)} \int_0^\infty \frac{z^{1/2} dz}{e^{z+\alpha} - 1}.$$ (26.12)

This is the expression for evaluating α: for later use it can be conveniently rewritten by defining

$$y \equiv \frac{n h^3}{V p_s (2\pi m kT)^{3/2}},$$ (26.13)

$$U(\alpha, \tfrac{1}{2}) \equiv \frac{1}{\Gamma(\tfrac{1}{2} + 1)} \int_0^\infty \frac{z^{1/2} dz}{e^{z+\alpha} - 1}.$$ (26.14)

After rearranging, (26.12) then becomes

$$y = U(\alpha, \tfrac{1}{2}).$$ (26.15)

To obtain the total energy of the gas (26.10) must be multiplied by ϵ and then integrated between zero and infinity; thus

$$E = \int \epsilon \, dn = \frac{\pi 2^{5/2} m^{3/2} V p_s}{h^3} \int_0^\infty \frac{\epsilon^{3/2}}{e^{(\epsilon/kT)+\alpha} - 1} \, d\epsilon.$$

Substituting z for ϵ/kT

$$E = \frac{\pi 2^{5/2} m^{3/2} V p_s (kT)^{5/2}}{h^3} \int_0^\infty \frac{z^{3/2}}{e^{z+\alpha} - 1} \, dz.$$ (26.16)

Replacing $\tfrac{3}{4}\pi^{1/2}$ by $\Gamma(\tfrac{3}{2} + 1)$ and substituting (26.13),

$$E = \tfrac{3}{2} kT \frac{n}{y \Gamma(\tfrac{3}{2} + 1)} \int_0^\infty \frac{z^{3/2}}{e^{z+\alpha} - 1} \, dz.$$ (26.17)

---

[1] The development under the next three subheadings follows that given by Tolman, *The Principles of Statistical Mechanics*, Oxford (1938).

* For the meaning of $\Gamma(x)$ see Whittaker and Watson, *Modern Analysis*, Fourth Edition, Cambridge University Press (1935), Chapter XII.

Writing

$$U(\alpha, \tfrac{3}{2}) \equiv \frac{1}{\Gamma(\tfrac{3}{2} + 1)} \int_0^\infty \frac{z^{3/2}}{e^{z+\alpha} - 1}\, dz, \qquad (26.18)$$

$$E = \tfrac{3}{2} nkT \frac{U(\alpha, \tfrac{3}{2})}{U(\alpha, \tfrac{1}{2})}. \qquad (26.19)$$

In order to investigate the pressure of the gas we take a cubical container of it with sides of length $V^{1/3}$. Consider the molecules in the energy range between ϵ and $\epsilon + d\epsilon$; as the motion is spherically symmetrical it will be correct to consider one third of the molecules as moving in directions parallel to each of the three edges of the container. The molecules move in each of these directions, either forwards or backwards, with a speed given by (26.5) and therefore each collides with a single face

$$\frac{1}{2 V^{1/3}} \left(\frac{2\epsilon}{m}\right)^{1/2} \quad \text{times per second.}$$

Since the change of momentum for each impact is

$$2mc = 2^{3/2} m^{1/2} \epsilon^{1/2}, \qquad (26.20)$$

the total change in momentum at one wall of the container per second for the particles with energy in the range between ϵ and $\epsilon + d\epsilon$, which move parallel to one of the edges of the cube, is

$$\sum \Delta m\dot{x} = \frac{2}{3 V^{1/3}} \left[\frac{\pi 2^{5/2} m^{3/2} V p_s}{h^3} \frac{\epsilon^{3/2} d\epsilon}{e^{(\epsilon/kT)+\alpha} - 1} \right]. \qquad (26.21)$$

The total change in momentum at one wall can be obtained by integrating between zero and infinity. Noting that after integration, the expression in the square brackets is the total energy E, the total change in momentum at one wall is found to be

$$\frac{2}{3 V^{1/3}} E = P V^{2/3}. \qquad (26.22)$$

In equation (26.22) the change in momentum per second at one wall has been equated to the total force exerted on a face of the cube (pressure $\times$ area of face); thus

$$P = \frac{2}{3} \cdot \frac{E}{V} = \frac{nkT}{V} \cdot \frac{U(\alpha, \tfrac{3}{2})}{U(\alpha, \tfrac{1}{2})}. \qquad (26.23)$$

For a condition of *slight gas degeneration*, equations (26.19) and (26.23) can be considerably simplified. Under such a condition α is small enough so that (22.14) does not reduce to the Maxwell-Boltzmann case but is still sufficiently

large that the integrals $U(\alpha, \frac{1}{2})$ and $U(\alpha, \frac{3}{2})$ can be expanded in rapidly converging power series, viz.,

$$U(\alpha, \tfrac{1}{2}) = e^{-\alpha} + \frac{e^{-2\alpha}}{2^{3/2}} + \frac{e^{-3\alpha}}{3^{3/2}} \cdots, \tag{26.24}$$

$$U(\alpha, \tfrac{3}{2}) = e^{-\alpha} + \frac{e^{-2\alpha}}{2^{5/2}} + \frac{e^{-3\alpha}}{3^{5/2}} \cdots. \tag{26.25}$$

It is then convenient to equate the right-hand side of (26.24) to y and to solve for $e^{-\alpha}$; thus

$$e^{-\alpha} = y \left\{ 1 - \frac{1}{2^{3/2}} y + \left(\frac{1}{4} - \frac{1}{3^{3/2}} \right) y^2 - \cdots \right\}. \tag{26.26}$$

This value of $e^{-\alpha}$ can then be substituted into (26.25) to obtain $U(\alpha, \frac{3}{2})$ as a function of y. Substituting this value into (26.23) and setting $U(\alpha, \frac{1}{2})$ equal to y the result is

$$P = \frac{nkT}{V} (1 - 0.1768y - 0.0033y^2 - \cdots). \tag{26.27}$$

Similarly from (26.19) we obtain

$$E = \tfrac{3}{2} nkT (1 - 0.1768y - 0.0033y^2 - \cdots). \tag{26.28}$$

Equation (26.27) tells us that for the pressure to deviate 0.8 per cent from the ordinary perfect gas law y must have the value 0.05 or

$$\frac{nh^3}{Vp_s(2\pi mkT)^{3/2}} = 0.05. \tag{26.29}$$

For hydrogen at standard temperature and pressure y is shown to be of the order of 10^{-5}, by substitution in the identity (26.13).

Suppose we are dealing with gaseous helium, for which p_s is unity (no spin). At 4° K, the normal boiling point of helium,

$$\frac{h^3}{p_s(2\pi mkT)^{3/2}} = 8.2 \times 10^{-23}$$

and for the case where $y = 0.05$, substituting in (26.29)

$$n/V = 0.61 \times 10^{21}.$$

Calculated on the basis of the perfect gas law, this value of n/V corresponds to a pressure of about 0.33 atm. of gaseous helium. Thus it is seen that gaseous helium at the normal boiling point gives pressures about 0.8 per cent less than the perfect gas law, due to gas degeneration, when the pressure is 0.33 atm.

Inasmuch as the pressure in an ordinary helium thermometer is of the order of 0.02 atm. at 4° K the effect is only about 0.05 per cent, or about 0.002° K compared with a correction for gas imperfection due to other causes of the order of 0.01° K. Thus even at 4° K effects due to gas degeneration are negligible compared with other causes of imperfection. At 1° K the effect at 1 atm. would be about 18 per cent of the pressure. However, the pressure of helium attainable without condensation is considerably less than 1 mm. at this temperature, so that the effect cannot be observed.

(27) **The Energy, Pressure and Heat Capacity of a Degenerate Gas Obeying the Fermi-Dirac Distribution Law:** The treatment is similar to that used in the Einstein-Bose case except that (23.7) is used in place of (22.14). The results obtained differ in that $U(\alpha, \frac{1}{2})$ and $U(\alpha, \frac{3}{2})$ are replaced by $V(\alpha, \frac{1}{2})$ and $V(\alpha, \frac{3}{2})$ where

$$V(\alpha, \tfrac{1}{2}) = \frac{1}{\Gamma(\tfrac{1}{2} + 1)} \int_0^\infty \frac{z^{1/2}dz}{e^{z+\alpha} + 1}, \tag{27.1}$$

$$V(\alpha, \tfrac{3}{2}) = \frac{1}{\Gamma(\tfrac{3}{2} + 1)} \int_0^\infty \frac{z^{3/2}}{e^{z+\alpha} + 1}. \tag{27.2}$$

Thus for a gas obeying the Fermi-Dirac distribution law

$$E = \tfrac{3}{2}nkT \frac{V(\alpha, \tfrac{3}{2})}{V(\alpha, \tfrac{1}{2})}, \tag{27.3}$$

$$P = \frac{nkT}{V} \cdot \frac{V(\alpha, \tfrac{3}{2})}{V(\alpha, \tfrac{1}{2})}. \tag{27.4}$$

For the case of slight degeneration we can make use of the power series expansions of $V(\alpha, \frac{1}{2})$ and $V(\alpha, \frac{3}{2})$. These are

$$V(\alpha, \rho) = e^{-\alpha} - \frac{e^{-2\alpha}}{2^{\rho+1}} + \frac{e^{-3\alpha}}{3^{\rho+1}} - \frac{e^{-4\alpha}}{4^{\rho+1}} + \cdots \tag{27.5}$$

with ρ equal to $\frac{1}{2}$ and $\frac{3}{2}$ respectively. Proceeding exactly as in the Einstein-Bose case

$$E = \tfrac{3}{2}nkT(1 + 0.176y - 0.0033y^2 + \cdots), \tag{27.6}$$

$$P = \frac{nkT}{V} (1 + 0.176y - 0.0033y^2 + \cdots) \tag{27.7}$$

with y given by (26.13). Thus at any attainable temperatures a gas composed of atoms and molecules has the energy and pressure calculated from the Boltzmann distribution law.

For the case of extreme degeneration we note that α in equation (23.7) may have a negative value whereas this is not possible in the Einstein-Bose case as the number of molecules in any state would become negative.

For negative values of α the expansion given by (27.5) is no longer valid. In that case Sommerfeld [1] has shown that

$$V(\alpha, \rho) = \frac{(-\alpha)^{\rho+1}}{\Gamma(\rho+2)}\left[1 + 2\left\{\frac{(\rho+1)\rho c_2}{\alpha^2} + \frac{(\rho+1)\rho(\rho-1)(\rho-2)c_4}{\alpha^4}\right\} + \cdots\right] \quad (27.8)$$

with the constants c_2, c_4, etc., given by

$$c_\nu = 1 - \tfrac{1}{2}^\nu + \tfrac{1}{3}^\nu - \tfrac{1}{4}^\nu. \quad (27.9)$$

The series in (27.8) converges rapidly when $-\alpha \gg 1$ and involves an approximation of the order of e^α.

Before substituting in the numerators of (27.3) and (27.4) the power series expansion of $V(\alpha, \tfrac{3}{2})$, according to (27.8), the series is expressed in terms of y. To do this we substitute for α, its value in terms of y, which is obtained using the equation

$$y = V(\alpha, \tfrac{1}{2}). \quad (27.10)$$

The value of α is given by

$$-\alpha = \left(\frac{3\sqrt{\pi}}{4}y\right)^{2/3}\left\{1 - \frac{\pi^2}{12}\left(\frac{4}{3y\sqrt{\pi}}\right)^{4/3}\right\}. \quad (27.11)$$

Now y is substituted for $V(\alpha, \tfrac{1}{2})$ in (27.3) and $V(\alpha, \tfrac{3}{2})$ is expressed in the form of (27.8), after substituting for α its value as given by (27.11); the procedure is the same for (27.4). The results obtained are respectively

$$E = n\frac{3h^2}{10m}\left(\frac{3n}{4\pi V p_s}\right)^{2/3} + n\frac{\pi^2 mk^2}{2h^2}\left(\frac{4\pi V p_s}{3n}\right)^{2/3}T^2 + \cdots, \quad (27.12)$$

$$P = \frac{n}{V}\cdot\frac{h^2}{5m}\left(\frac{3n}{4\pi V p_s}\right)^{2/3} + \frac{n}{V}\cdot\frac{\pi^2 mk^2}{3h^2}\left(\frac{4\pi V p_s}{3n}\right)^{2/3}T^2 + \cdots. \quad (27.13)$$

By differentiating (27.12) with respect to T,

$$C_v = \left(\frac{\partial E}{\partial T}\right)_V = n\frac{\pi^2 mk^2}{h^2}\left(\frac{4\pi V p_s}{3n}\right)^{2/3}T. \quad (27.14)$$

Thus we see that the heat capacity of a highly degenerate gas obeying the Fermi-Dirac statistics is proportional to the temperature when α has large negative values. Electrons with $s = \tfrac{1}{2}$ and $p_s = 2s + 1 = 2$ must have wave functions (including spin) which are antisymmetric. The above results can thus be applied to electron gas.

(28) **The Heat Capacity due to Free (Conducting) Electrons in Metals:** For the element silver, we shall assume that there is one free electron in the metal for each atom and that the electric conductivity is entirely due to such

[1] Sommerfeld, *Z. Physik*, **47**, 1 (1928).

electrons which behave as a gas. It is simple to compute y. The number of electron spin states ($s = \frac{1}{2}$) is

$$p_s = 2s + 1 = 2, \tag{28.1}$$

and so it follows from (26.13) that

$$y = 2,200 \tag{28.2}$$

at 300° K, and from (27.11)

$$\alpha = -205. \tag{28.3}$$

Evidently e^α is negligible and series like (27.8) are convergent so that the case is one of extreme degeneracy. Thus at ordinary temperature the heat capacity due to conducting electrons in silver is given by (27.14) and

$$C_v = 0.767 \times 10^{-4} nkT \tag{28.4}$$

or

$$C_v = 0.767 \times 10^{-4} RT = 1.53 \times 10^{-4} T \text{ calories per gram atom,} \tag{28.5}$$

$$= 0.046 \text{ calories per gram atom at 300° K.} \tag{28.6}$$

This is to be added to the Dulong and Petit value of $3R$ to obtain the total heat capacity, at constant volume, of silver.

If the electrons in silver behaved as a perfect classically excited gas, the contribution due to the electrons would be $3R/2$. It was one of the early objections to Drude's theory (that conducting electrons in metals behaved as a gas) that the total value of C_v found for metals like silver was $3R$ and not $(3 + \frac{3}{2})R$ as would have been predicted from his theory. The advent of the quantum theory has removed these objections as can be seen from (28.6) which predicts a total value of C_v only 0.8 per cent higher than the Dulong and Petit value.

This difference is barely outside the error of existing determinations of C_v. It remained for Keesom and Kok [1] to demonstrate the validity of equation (27.14). They made use of the fact that, at low temperatures, the Debye contribution to the heat capacity varies as the cube of the temperatures whereas the contribution of the electrons varies as the first power. Thus at low temperatures the contribution of the conducting electrons to the heat capacity should become of the same order of magnitude as the Debye contribution. They found that for silver the heat capacity remaining after subtracting the Debye contribution follows equation (28.5).

(29) **Limit of Applicability of the Maxwell Distribution Law:** It has been seen in Section (24) that the Einstein-Bose and Fermi-Dirac distribution laws reduce to the Maxwell-Boltzmann distribution in the form

$$n_k = p_k e^{-\alpha} e^{-\epsilon_k/kT} \tag{29.1}$$

for large values of α. This will be true whenever the denominator in equations

<hr>

[1] Keesom and Kok, *Physica*, 1, 770 (1934); *Proc. Acad. Sci. Amsterdam*, **37**, 377 (1934); Keesom and Clark, *Physica*, 2, 698 (1935).

(22.14) and (23.7) is large compared with unity for all energy states present in appreciable numbers. The most unfavorable case will involve those states for which ϵ/kT approaches zero; for these e^α must be large compared with unity.

For helium at $4°$ K and 0.33 atm. pressure we have seen that $y = 0.05$. By equation (26.26)

$$e^\alpha \sim 1/y = 20. \tag{29.2}$$

Thus equation (29.1) will be correct to five per cent even for the lowest energy states. At $16°$ K and the same pressure, y is about 0.0016 and e^α is about 600 so that the error has been reduced to about 0.16 per cent. It is thus evident that equation (29.1) will be correct except at the lowest temperatures and reasonably correct for all gases above $4°$ K.

The number of states, p_k, corresponding to the volume in the μ-space $dxdydzd(m\dot{x})d(m\dot{y})d(m\dot{z})$ is

$$p_k = \frac{p_s dxdydzd(m\dot{x})d(m\dot{y})d(m\dot{z})}{h^3} \tag{29.3}$$

and, according to (29.1), the number of molecules in these states is

$$dn = C p_s m^3 e^{-\epsilon k/kT} dxdydzd\dot{x}d\dot{y}d\dot{z}/h^3, \tag{29.4}$$

where C has been written for $e^{-\alpha}$. Evidently the value of C is given by

$$C = e^{-\alpha} = \frac{nh^3}{p_s m^3 V \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-m(\dot{x}^2+\dot{y}^2+\dot{z}^2)/2kT} d\dot{x}d\dot{y}d\dot{z}}$$

$$= \frac{nh^3}{p_s V(2\pi mkT)^{3/2}}, \tag{29.5}$$

in which V is the result of the integration over the volume of the container. The translational partition function in the classical limit is

$$Q_t = \frac{p_s m^3 V}{h^3} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-m(\dot{x}^2+\dot{y}^2+\dot{z}^2)/2kT} d\dot{x}d\dot{y}d\dot{z}$$

$$= \frac{p_s V(2\pi mkT)^{3/2}}{h^3}, \tag{29.6}$$

or, substituting NkT/P for V,

$$Q_t = \frac{p_s N(2\pi m)^{3/2}(kT)^{5/2}}{h^3 P}. \tag{29.7}$$

(30) **Thermodynamic Analogies: The Boltzmann Relation Between Entropy and Probability:** When an isolated system undergoes a spontaneous change, the entropy increases and the system passes towards a more probable state. Thus there is evidently a connection between entropy and probability.[1]

---

[1] Boltzmann, Vorlesungen über Gastheorie, Barth, Leipzig (1912). Lewis and Randall, Thermodynamics, McGraw-Hill, New York (1923), p. 120.

When we say that a system in a given state has a probability W, we mean that if a system is withdrawn from a large number of similar systems it has a fractional chance, W, of being in that state as compared to unity that it will be in any one of all the possible states. Let us take two systems, of probabilities W_1 and W_2, and entropies S_1 and S_2, from the assembly and combine them. The combined probability of the systems is W_1W_2, since probabilities are multiplicative. On the other hand the entropies of the systems are additive. The only type of functional relation that will satisfy these considerations is that

$$S = K \ln W + \text{const.,} \qquad (30.1)$$

where the additive constant gives the value of the entropy corresponding to $W = 1$. For equation (30.1) to be applicable it is necessary to find the value of K. This can be done readily by considering the case of the expansion of one mole of a perfect gas from a pressure P_1 to a pressure P_2 by expanding from one container of volume v_1 into another of volume v_2 such that

$$v_1/(v_1 + v_2) = P_2/P_1. \qquad (30.2)$$

With the containers connected the chance, w_1, that a single molecule will be in the container of volume v_1 rather than in the total volume $v_1 + v_2$ is

$$w_1 = v_1/(v_1 + v_2). \qquad (30.3)$$

The corresponding chance, W_1, that all N molecules (where N is the Avogadro number) will lie in the volume v_1 is

$$W_1 = \left(\frac{v_1}{v_1 + v_2} \right)^N . \qquad (30.4)$$

The chance W_2 of finding the molecules in the volume $v_1 + v_2$ is, of course, unity. Let the entropy before expansion be S_1 and after expansion S_2. Applying equation (30.1)

$$S_2 - S_1 = K \ln \left(\frac{W_2}{W_1} \right) = K \ln \left(\frac{v_1}{v_1 + v_2} \right)^{-N} = K \ln \left(\frac{v_1 + v_2}{v_1} \right)^N . \quad (30.5)$$

However, from elementary thermodynamics (see Chapter III) the entropy increase on expansion from v_1 to $v_1 + v_2$ is

$$S_2 - S_1 = R \ln \left(\frac{v_1 + v_2}{v_1} \right) = k \ln \left(\frac{v_1 + v_2}{v_1} \right)^N , \qquad (30.6)$$

where $k = R/N$ is the Boltzmann gas constant. Comparing (30.5) and (30.6) we see that $K = k$. Thus equation (30.1) becomes

$$S = k \ln W + \text{const.} \qquad (30.7)$$

This is the Boltzmann relation between entropy and probability.

It is not necessary to inquire into the value that is to be assigned to the additive constant if only entropy differences are involved.   Thus we shall use equation (30.7) in the form

$$S_2 - S_1 = k \ln (W_2/W_1) \tag{30.8}$$

and only be interested in ratios of probabilities.   The probability of finding the system in a given *macroscopic* state is proportional to the number of *microscopic* states which correspond to it, each of which has the same probability.

It is the convention to assign zero entropy to perfect crystals at the absolute zero since all have the same entropy.   At the absolute zero every particle is in its lowest quantum state and the system is one of localized particles.   For example, if a crystal of an element had one atom of a radioactive isotope at a particular point in the lattice it would be found that the radioactive atom would stay at that point.   Evidently the state of a particular perfect crystal at the absolute zero is represented by one and only one microscopic state and it is clear why each has the same entropy.   It is true that reconstruction of the crystal from its particles would give a different arrangement of particles. However, we would not regard the new arrangement as giving rise to a different region in the γ-space because, apart from the positions which they occupy, the particles have no identity and the new crystal is not distinguishable from the old in any way.   If it were physically possible to have a very mobile crystal at the absolute zero in which the particles could change places rapidly, such a crystal would correspond only to one microscopic state because of the indistinguishability of the particles; it would thus have the same entropy as the perfect crystal of localized particles.

It is thus natural to assign zero entropy to a system defined by a single microscopic state: hence the entropy of a system is given by

$$S = k \ln P, \tag{30.9}$$

where P is the number of microscopic states, each of which represent, i.e., correspond to, the state of the system.   It is possible to show that, quite generally, the entropy thus defined satisfies all the thermodynamic requirements.[1]   An ingenious way of doing this has been given by Sommerfeld.[2]   For constant temperature and pressure the volume, energy, entropy and free energy are proportional to the number of molecules in the system: let us write

$$V = nv, \tag{30.10}$$

$$E = nu, \tag{30.11}$$

$$S = ns, \tag{30.12}$$

$$F = n\mu,$$

---

[1] Planck, *Z. Physik*, **35**, 155 (1926).   Lewis and Mayer, *Proc. Nat. Acad. Sci.*, **14**, 569 (1928) and succeeding article.

[2] Sommerfeld, *Z. Physik*, **47**, 1 (1928).

where n is the number of molecules in the system. The free energy is defined by

$$F = E + PV - TS, \qquad (30.13)$$

so that

$$\mu = u + Pv - Ts, \qquad (30.14)$$

where μ is the molal free energy divided by the Avogadro number. Noting that

$$du = Tds - Pdv$$

by the application of the first and second laws to a system with n constant,

$$dS = d(ns) = nds + sdn$$

$$dS = n \cdot \frac{du + Pdv}{T} + sdn$$

$$= \frac{dE + PdV}{T} - \frac{u + Pv}{T} dn + sdn$$

$$= \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dn. \qquad (30.15)$$

Thus

$$\left(\frac{\partial S}{\partial E} \right)_{V,n} = \frac{1}{T}, \qquad (30.16)$$

$$\left(\frac{\partial S}{\partial V} \right)_{E,n} = \frac{P}{T}, \qquad (30.17)$$

$$\left(\frac{\partial S}{\partial n} \right)_{E,V} = - \frac{\mu}{T}. \qquad (30.18)$$

The derivations of the distribution laws (29.1), (22.14) and (23.7) had an expression in common, namely,

$$- \delta \ln P + \sum_k (\beta \epsilon_k + \alpha) \delta n_k = 0. \qquad (30.19)$$

Using (30.9) and noting that β and α are constants this equation becomes

$$- \frac{\delta S}{k} + \beta \sum \epsilon_k \delta n_k + \alpha \sum \delta n_k = 0 \qquad (30.20)$$

or

$$- \frac{1}{k} \delta S + \beta \delta E + \alpha \delta n = 0, \qquad (30.21)$$

whence

$$\delta S = k\beta \delta E + k\alpha \delta n. \qquad (30.22)$$

Thus

$$\left(\frac{\partial S}{\partial E} \right)_{V,n} = k\beta \qquad (30.23)$$

and

$$\left(\frac{\partial S}{\partial n}\right)_{V,E} = k\alpha.^* \tag{30.24}$$

Comparing (30.23) with (30.16)

$$k\beta = \frac{1}{T} \quad \text{or} \quad \beta = \frac{1}{kT} \tag{30.25}$$

and from (30.24) and (30.18)

$$k\alpha = -\frac{\mu}{T}, \quad \alpha = -\frac{\mu}{kT}. \tag{30.26}$$

Thus the quantity as defined by (30.9) has been demonstrated to have the required properties of entropy. It is also to be noted that, in Section (13), β has been shown to be equal to $1/kT$, so that (30.25) may be regarded as a general demonstration that K in equation (30.5) is indeed the Boltzmann gas constant k. Equation (30.26) can be written

$$\alpha = -\frac{F}{nkT}$$

or

$$F = -nkT\alpha. \tag{30.27}$$

For a system which can be considered to obey the Boltzmann distribution law we have seen, by equations (20.1) and (21.1), that

$$\frac{1}{C} = \frac{Q}{n} = e^{\alpha}, \tag{30.28}$$

hence,

$$F = -nkT \ln \frac{Q}{n}. \tag{30.29}$$

This equation is deduced directly in the preceding chapter by an argument which does not involve the formal reasoning just employed and hence renders (30.27) less abstract.

(31) **The Entropy of Systems of Localized Elements—Rotational and Vibrational Entropy of Gases:** In Section (20) it was shown that rotational, vibrational and electronic degrees of freedom form localized elements which follow the Boltzmann distribution law. We shall consider a system of N particles (1 mole). The following derivation applies not only to rotational, vibrational and electronic degrees of freedom of the molecules in a gas, but also to the internal vibrations of the molecules in a crystal. This separation of rotational and vibrational degrees of freedom from the translational degrees of freedom is only possible when the latter are statistically independent. This

---

* It should be noted carefully that, in the original expression for P, n must be regarded as variable.

will be true when α is reasonably large in the Einstein-Bose or Fermi-Dirac expression for the translational distribution although it is not necessarily large enough to cause degeneration to vanish even approximately.[1]

The number of microscopic states corresponding to a macroscopic state is given by

$$P = \frac{N!}{n_1! n_2! \cdots n_k!},$$ (31.1)

where the subscript $1, 2, \cdots, k$ stand for all the quantum numbers of the set. The entropy of the system is therefore given by

$$S = k \ln \frac{N!}{n_1! n_2! \cdots n_k!} = k(N \ln N - N - \sum_j n_j \ln n_j - \sum_j n_j)$$
$$= k(N \ln N - \sum_j n_j \ln n_j) \quad (31.2)$$

after noting that $\sum_j n_j$ is equal to N. Equation (31.2) may be rewritten

$$S = k(\sum_j n_j \ln N - \sum_j n_j \ln n_j),$$ (31.3)

$$= - k \sum_j n_j \ln (n_j/N),$$ (31.4)

$$= - R \sum_j \frac{n_j}{N} \ln \left(\frac{n_j}{N} \right).$$ (31.5)

Substituting for n_j/N its value from (20.5) with Q defined by (21.1)

$$S = - R \sum_j \frac{e^{-\epsilon_j/kT}}{Q} \ln \frac{e^{-\epsilon_j/kT}}{Q}$$
$$= R \left[\sum_j \frac{e^{-\epsilon_j/kT}}{Q} \ln Q + \sum_j \frac{\epsilon_j}{kTQ} e^{-\epsilon_j/kT} \right]$$
$$= R \left[\left(\frac{\ln Q}{Q} \right) \sum_i p_i e^{-\epsilon_i/kT} + \left(\frac{1}{kTQ} \right) \sum_i p_i \epsilon_i e^{-\epsilon_i/kT} \right], \quad (31.6)$$

where i stands only for the quantum numbers which determine the energy and p_i is the number of states with the energy ϵ_i. Noting the definition of Q

$$S = R \left[\ln Q + \left(\frac{1}{kTQ} \right) \sum_i p_i \epsilon_i e^{-\epsilon_i/kT} \right]$$ (31.7)

or

$$S = R \left[\ln Q + T \frac{\partial \ln Q}{\partial T} \right],$$ (31.8)

$$S = R \frac{\partial(T \ln Q)}{\partial T},$$ (31.9)

[1] See Tolman, The Principles of Statistical Mechanics, The Clarendon Press, Oxford (1938), page 517, for an excellent discussion.

or

$$S = R \left[\ln Q - \frac{1}{TQ} \cdot \frac{\partial Q}{\partial (1/T)} \right], \tag{31.10}$$

$$S = R \left[\ln Q - \frac{1}{T} \left(\frac{Q'}{Q} \right) \right], \tag{31.11}$$

where

$$Q' = \frac{\partial Q}{\partial (1/T)} . \tag{31.12}$$

Equation (31.7) can also be put in the form

$$S = R \ln Q + E/T, \tag{31.13}$$

where

$$E = \frac{N \sum_i p_i \epsilon_i e^{-\epsilon_i/kT}}{\sum_i p_i e^{-\epsilon_i/kT}} , \tag{31.14}$$

which can be seen to be the energy per gram mole of the system.

Equations (31.7), (31.8), (31.9) and (31.11) are equivalent general expressions for the entropy of a localized system which can be applied to the rotational, vibrational, and electronic states of a system of molecules or to the vibrational modes of a crystal.

(32) **The Translational Entropy—The Sackur-Tetrode Equation:** In deriving the expression for the entropy of a gas when the translation is classically excited in the sense that (29.1) holds, there are two possibilities to consider: (1) when the wave functions are symmetrical, and (2) when they are antisymmetrical. For the former we have by equation (22.6)

$$\ln \boldsymbol{P} = \sum n_k \ln (1 + p_k/n_k) + \sum p_k \ln (1 + n_k/p_k), \tag{32.1}$$

while for the latter, by expanding $\ln \boldsymbol{P}$ with $\boldsymbol{P}$ given by (23.3) we obtain

$$\ln \boldsymbol{P} = \sum n_k \ln (p_k/n_k - 1) - \sum p_k \ln (1 - n_k/p_k). \tag{32.2}$$

If α is large, $e^{-(\beta\epsilon_k+\alpha)}$ is small compared to unity

$$n_k/p_k = e^{-(\beta\epsilon_k+\alpha)} \ll 1 \tag{32.3}$$

and

$$p_k/n_k = e^{(\beta\epsilon_k+\alpha)} \gg 1. \tag{32.4}$$

In both (32.1) and (32.2) $\ln (1 \pm n_k/p_k)$ can be replaced by n_k/p_k because of (32.3), and unity can be neglected compared to p_k/n_k in the argument of the logarithm of the first term because of (32.4); hence

$$S_t = k \ln \boldsymbol{P} = k \sum n_k \ln (e^{\beta\epsilon_k+\alpha}) + kn \tag{32.5}$$

gives the translational entropy, or

$$S_t = k \sum_k n_k(\beta\epsilon_k + \alpha) + kn, \tag{32.6}$$

in which kn has been substituted for $k \sum_k n_k$. According to (24.1)

$$n_k = p_k e^{-\alpha} e^{-\beta \epsilon_k} \tag{32.7}$$

and we may substitute for p_k in this expression the number of quantum states between ϵ and $\epsilon + d\epsilon$ as given by (26.9); thus

$$n_k \equiv dn = \frac{\pi 2^{5/2} m^{3/2} V p_s}{h^3} e^{-\alpha} \epsilon^{1/2} e^{-\epsilon/kT} d\epsilon. \tag{32.8}$$

From equation (29.5)

$$e^{-\alpha} = \frac{nh^3}{(2\pi mkT)^{3/2} V p_s} \tag{32.9}$$

and so it follows that

$$dn = \frac{2n}{\pi^{1/2}(kT)^{3/2}} \epsilon^{1/2} e^{-\epsilon/kT} d\epsilon. \tag{32.10}$$

Substituting this result into (32.6)

$$S_t = k \int_0^\infty \frac{2n}{\pi^{1/2}(kT)^{3/2}} \cdot \frac{\epsilon^{3/2}}{kT} e^{-\epsilon/kT} d\epsilon + kn\alpha + kn, \tag{32.11}$$

but since

$$\int_0^\infty \epsilon^{5/2} e^{-\epsilon/kT} d\epsilon = (kT)^{5/2} \frac{3\pi^{1/2}}{4},$$

equation (32.11) becomes

$$S_t = nk \ln \frac{(2\pi mkT)^{3/2} V p_s}{nh^3} + \tfrac{5}{2} nk. \tag{32.12}$$

Substituting

$$V = nkT/P$$

we obtain the translational entropy for one mole of gas (for which $n = N$),

$$S_t = \tfrac{5}{2} R + \tfrac{5}{2} R \ln T - R \ln P + R \ln \frac{(2\pi m)^{3/2} k^{5/2} p_s}{h^3}, \tag{32.13}$$

which is the Sackur-Tetrode equation. The factor p_s in the argument of the logarithm of the constant term is the number of electron spin or nuclear spin states of equal energy not counted when calculating the entropy of other degrees of freedom. The nuclear spin in molecular hydrogen would not be included as it is taken into account in calculating the rotational entropy. It will be noted that equation (32.12) can be put in the form

$$S_t = R[\ln Q_t/N + T(\partial \ln Q_t/\partial T)_P]. \tag{32.14}$$

Before the partial differentiation, Q_t must be expressed in the form given in equation (29.7).

Had equation (32.14) been derived considering all degrees of freedom of a system of molecules, i.e., considering the total wave function of the molecules, an expression exactly like (32.14) would have been obtained for the total entropy of one mole of gas, viz.,

$$S = R \left[\ln \frac{Q_{\text{total}}}{N} + T \left(\frac{\partial \ln Q_{\text{total}}}{\partial T} \right)_P \right] \tag{32.15}$$

with Q_{total} given by

$$Q_{\text{total}} = Q_t \times Q_{\text{int.}}, \tag{32.16}$$

where

$$Q_{\text{int.}} = \sum_i p_i e^{-\epsilon_i/kT} \tag{32.17}$$

is the partition function for the internal (including external rotational) degrees of freedom, the sum being taken over all quantum states. However, equation (32.15) follows directly and generally from (30.29) by using $S = -(\partial F/\partial T)_P$. Equation (32.15) can be separated into two equations, namely, (32.14) and

$$S_{\text{int.}} = R \left[\ln Q_{\text{int.}} + T \frac{\partial \ln Q_{\text{int.}}}{\partial T} \right] \tag{32.18}$$

as is evident from the logarithmic nature of the terms in (32.15). Equation (32.18) is a special case of equation (31.8) and gives the entropy due to rotational, vibrational, and electronic states (if more than one).

The partition function $Q_{\text{int.}}$ may also include the nuclear spin partition function if nuclear spin is not otherwise allowed for, as seen below.

NUCLEAR SPIN EFFECTS

(33) **The Entropy due to Nuclear Spin:** According to the new quantum mechanics only quantum states are allowed whose total wave function is either symmetric or antisymmetric in the nuclei depending on whether the nuclei have an even or odd mass number (even or odd number of protons and neutrons).

Consider a gas made up of diatomic molecules containing equivalent nuclei with i units of spin angular momentum. Each nucleus has $n = 2i + 1$ spin wave functions of essentially equal energy. Let these be $\chi_1, \chi_2, \chi_3, \cdots, \chi_n$ for one nucleus and $\phi_1, \phi_2, \phi_3, \cdots, \phi_n$ for the other, where χ_1 is identical with ϕ_1, etc. The allowed spin wave functions for the molecule are made up of linear combinations of the products of these. First there are the n spin wave functions $\phi_1\chi_1, \phi_2\chi_2, \phi_3\chi_3, \cdots, \phi_n\chi_n$ which are totally symmetric, since interchanging nuclei between the identical wave functions does not change the sign of the function. Then there are the $n(n - 1)/2$ spin wave functions of the type $\phi_1\chi_2 + \phi_2\chi_1$ (or in general $\phi_i\chi_j + \phi_j\chi_i$) which also do not change sign when nuclei are interchanged and are totally symmetric. Thus the number of totally symmetric wave functions is the sum of the two kinds, namely $n(n + 1)/2$. Finally there are the spin wave functions of the type $\phi_i\chi_j - \phi_j\chi_i$ whose sign changes when the nuclei are exchanged. These are antisymmetric and there

are $n(n - 1)/2$ of them. The total number of nuclear spin wave functions is evidently $n^2 = (2i + 1)^2$.

The nuclear spin wave functions of the symmetric type are called ortho states while the antisymmetric ones are called para states. For nuclei with an even mass number, ortho nuclear states will require rotational states for the molecule symmetric in the nuclei, and para will require rotational states antisymmetric in the nuclei in order to keep the total nuclear wave function symmetric. For nuclei of odd mass number exactly the opposite requirement exists to keep the total nuclear wave function antisymmetric. The rotational states symmetric in the nuclei have even rotational quantum numbers (J) while the antisymmetric states have odd quantum numbers. Thus for homonuclear molecules made up of nuclei of even mass number there are $n(n + 1)/2$ symmetric nuclear spin wave functions which are confined to even rotational states and $n(n - 1)/2$ antisymmetric nuclear spin wave functions confined to odd rotational states. For nuclei of odd mass number exactly the opposite situation exists. Nitrogen and deuterium are examples of the first case and the chlorine isotopes and hydrogen of the second.

It is not possible for nuclear spin wave functions to change one into another in the absence of magnetic interaction; hence any diatomic gas consists of $n^2 = (2i + 1)^2$ kinds of molecules differentiated by their nuclear spin wave functions. Of these kinds, $n(n + 1)/2$ have the one set of rotational states (even or odd), and $n(n - 1)/2$ have the other. These may all be regarded as different gases. Actually over a long time, in any container, there will be a change of one spin wave function into another, so that a diatomic gas as a rule has the ratio of ortho to para states which is that demanded for statistical equilibrium at room temperature. For all cases except hydrogen and deuterium, and for these to a reasonable degree of approximation, room temperature corresponds to essentially classical conditions. Thus each one of the gases will have the same energy, entropy, and free energy as can be seen by referring to equation (32.18) for the rotational and vibrational entropy. For the ortho type molecules the sums in the partition function are taken over even (or odd) rotational levels, and for the para type they are taken over odd (or even) levels. When classical conditions maintain, the sums over even levels equal those over odd levels as can be seen by summing the terms for odd and even rotational levels for hydrogen chloride subsequently given in Section (45). The rotational and vibrational entropies of ortho and para type molecules are therefore equal; the translational entropy is given by equation (32.13). Thus the total entropy is the same for both types; by a similar argument it can be shown that this is also true of the energy, heat capacity, and free energy.

Since all the types of molecules have the same free energy they are present in equal amounts. To obtain the total entropy one merely adds the entropy of mixing of the $(2i + 1)^2$ kinds of molecules to the entropy of any one kind. The total entropy including nuclear spin under classical conditions is consequently

$$S = S_t + S_{r+v} + R \ln (2i + 1)^2, \tag{33.1}$$

because each kind is present in a mole fraction of $1/(2i + 1)^2$. The term S_t is the translational entropy obtained from (32.13) while S_{r+v} is the rotational and vibrational entropy obtained from equation (32.18) by taking the sum in Q over all rotational states (even and odd J values) and dividing the result by two.

Under conditions when the wave functions cannot change into one another, the high temperature equilibrium mixture will persist. *The important point is that for all gases except hydrogen and deuterium the equilibrium ratio is still the classical one down to temperatures below those of liquid air within a reasonable degree of approximation.* Hence, for all gases except hydrogen and deuterium the distribution is an equilibrium one and the entropy is always given by equation (33.1). The situation with regard to hydrogen will be discussed in Sections (43) and (46).

The entropy of mixing of the $(2i + 1)^2$ nuclear spin wave functions, namely, $R \ln (2i + 1)^2$, can be looked upon as an entropy of $R \ln (2i + 1)$ for each nucleus with i units of spin.[1]

For all substances except hydrogen and deuterium, therefore, at all except low temperatures the entropy due to nuclear spin is simply the entropy of mixing of the nuclear spin wave functions.[2] Consider a molecule with atoms of nuclear spins i_1, i_2, i_3, $\cdots$, i_p; each nucleus has $2i_k + 1$ spin wave functions. There will thus be $(2i_1 + 1) (2i_2 + 1) \cdots (2i_p + 1)$ nuclear spin wave functions for the molecule and at high temperatures (classical distribution) the equilibrium mixture will contain the same fraction of the molecules with each wave function. The nuclear spin entropy under these conditions is the entropy of mixing of $(2i_1 + 1) (2i_2 + 1) \cdots (2i_p + 1)$ kinds of molecules in equal ratios, namely

$$S_s = R \ln (2i_1 + 1) (2i_2 + 1) \cdots (2i_p + 1) \tag{33.2}$$

or the contribution to the nuclear spin entropy is

$$(S_s)_k = R \ln (2i_k + 1) \tag{33.3}$$

for each atom. Thus the nuclear spin entropy will be the same for reactants and products of a chemical reaction since the same number of the several kinds of atoms occurs on both sides of the *chemical* equation.

Except, then, for hydrogen and deuterium gas it will be possible to neglect the nuclear spin entropy altogether. The value of the entropy of a substance which does not include the nuclear spin entropy is called the *practical entropy*. Obviously if tables of entropy are made up on this basis, the entropy of gaseous hydrogen (each nucleus with $i = \frac{1}{2}$) must be reduced by $R \ln 2^2$. In this exceptional case $R \ln 2^2$ is not the entropy due to nuclear spin but is the value of the nuclear spin entropy due to two atoms of hydrogen in all other cases. It is just this amount that is neglected for two atoms of hydrogen in all other

[1] Gibson and Heitler, *Z. Phyik*, **49**, 465 (1928).

[2] Mayer, Brunauer and Mayer, *J. Am. Chem. Soc.*, **55**, 37 (1933).

cases and therefore to ensure cancellation it must be neglected for gaseous hydrogen also.

First we wish to see whether or not the entropy obtained using the third law of thermodynamics and data down to liquid hydrogen temperatures (10° K) includes the nuclear spin entropy. Simple considerations show that it does not.

We have seen that states differing only in the nuclear spin wave functions have the same energy. In the crystal at low temperatures, a molecule with a given nuclear spin wave function will be in the lowest energy state for all the other degrees of freedom which will allow the total wave function to have the correct symmetry in the nuclei. Let us consider the case where the molecules with the different nuclear spin states are not in equilibrium but in the equal ratios obtained by their having been brought into equilibrium by formation at high temperatures. Instead of the crystal consisting of molecules in a single quantum state, it consists of equal amounts of $(2i_1 + 1)\ (2i_2 + 1)\ \cdots$ $(2i_p + 1)$ kinds of molecules *randomly* distributed throughout the crystal lattice differentiated by their total wave function. If the crystal were made up entirely of any one of these kinds our convention, previously established, would assign it zero entropy. Our actual crystal is now a solid solution, and moreover a perfect one if the interactions between the different kinds of molecules are the same. The entropy of the crystal is, therefore, the entropy of mixing of these different kinds of molecules

$$S = R \ln (2i_1 + 1)\ (2i_2 + 1) \cdots (2i_p + 1). \qquad (33.4)$$

This is exactly the nuclear spin entropy that we have already discussed, and so, if we make a third law calculation of the entropy of gas on the assumption that the actual crystal has zero entropy at the absolute zero, the entropy obtained does not include the nuclear spin entropy which really exists in the crystal down to the absolute zero. As an example of this, the entropy of nitrogen in the ideal gas state calculated according to equation (33.1) *but neglecting the term $R \ln 9$* is 36.42 cal. per deg. per mole at 77.32° K and one atmosphere. The entropy calculated from calorimetric data and the third law, and corrected to the ideal gas state, is 36.5 cal. per deg. per mole.

<center>GASES</center>

(34) **The General Expression for Energy and Heat Capacity:** It has already been shown that the translational degrees of freedom of a molecule are separable from the other degrees of freedom (rotation and vibration). The energy of an ideal gas due to classically excited translation has been found to be

$$E_t = \tfrac{3}{2}RT. \qquad (34.1)$$

The corresponding heat capacities at constant volume and constant pressure were found to be

$$(C_t)_v = \tfrac{3}{2}R \qquad (34.2)$$

and

$$(C_t)_p = \tfrac{5}{2}R. \tag{34.3}$$

and from the considerations in Section (29), these expressions should hold for all ideal gases above 30° K.

It remains to consider the energy and heat capacity due to the rotational, vibrational and electronic degrees of freedom all of which, in general, will be quantized. We shall, therefore, derive general expressions for the energy and heat capacity due to a number of quantized degrees of freedom whose energies may not be separable.

From equation (20.6) it can easily be seen that the total energy per mole is

$$E = \frac{N \sum_i p_i \epsilon_i e^{-\epsilon_i/kT}}{\sum_i p_i e^{-\epsilon_i/kT}} = N\bar{\epsilon}, \tag{34.4}$$

where i stands for the set of quantum numbers that determine the energy, rotational, vibrational and (or) electronic. The average energy per molecule ($\bar{\epsilon}$) is E/N.

Let

$$Q' = \frac{\partial Q}{\partial(1/T)} = -\frac{1}{k}\sum_i p_i \epsilon_i e^{-\epsilon_i/kT}, \tag{34.5}$$

$$Q'' = \frac{\partial^2 Q}{\partial(1/T)^2} = +\frac{1}{k^2}\sum_i p_i \epsilon_i^2 e^{-\epsilon_i/kT}. \tag{34.6}$$

Then

$$E = -R\frac{Q'}{Q} = -R\frac{\partial \ln Q}{\partial(1/T)} \tag{34.7}$$

and

$$C = T\frac{\partial S}{\partial T} = \frac{\partial E}{\partial T} = \frac{R}{T^2}\cdot\frac{\partial(Q'/Q)}{\partial(1/T)} = \frac{R}{T^2}\cdot\frac{\partial^2 \ln Q}{\partial(1/T)^2} \tag{34.8}$$

or

$$C = \frac{R}{T^2}\left[\frac{Q''}{Q} - \left(\frac{Q'}{Q}\right)^2\right]. \tag{34.9}$$

Substituting (34.5) and (34.6) in (34.9)

$$C = \frac{N}{kT^2}\left[\frac{\sum \epsilon^2 p e^{-\epsilon/kT}}{\sum p e^{-\epsilon/kT}} - \left(\frac{\sum \epsilon p e^{-\epsilon/kT}}{\sum p e^{-\epsilon/kT}}\right)^2\right], \tag{34.10}$$

where the subscripts have been dropped for convenience.

(35)* **Approximate Methods for Evaluating the Partition Function and its Derivatives—Introduction:** Expressions have already been given for the energy, heat capacity and entropy in terms of the energy levels of rotational, vibrational

---

* In Sections (35) to (42), subscript v refers to "vibrational," and not to constant volume.

and electronic degrees of freedom; namely,

$$E = - R \frac{Q'}{Q}, \tag{34.7}$$

$$C = \frac{R}{T^2} \left[\frac{Q''}{Q} - \left(\frac{Q'}{Q} \right)^2 \right], \tag{34.9}$$

$$S = R(\ln Q - Q'/QT), \tag{31.11}$$

where Q' and Q'' denote the first and second derivatives of the partition functions with respect to $1/T$

$$Q' = dQ/d(1/T) = - T^2 dQ/dT; \quad Q'' = T^2[T^2(d^2Q/dT^2) + 2T(dQ/dT)].$$

It is desirable to set up a simple expression for Q in terms of the observed energy levels in which the cumbersome sum of exponentials has been eliminated. It is further desirable to have the expression an explicit function of $1/T$ (or T) so that Q' and Q'' can be obtained by straightforward differentiation. All approximate methods of obtaining thermodynamic functions directly from the energy levels have this as their object. The first step in this direction was made by Mulholland [1] who gave an expression for Q_r applying to the rotational energy levels of a diatomic molecule in which the exponentials had been eliminated. The rotational energy of a rigid diatomic molecule can be expressed in the form

$$\epsilon = J(J + 1)Bhc,$$

where $B = h/8\pi^2 Ic$ and J can have the values 0, 1, 2, 3, 4, etc. Thus Q_r can be written

$$Q_r = \sum_{J=0}^{J=\infty} (2J + 1)e^{-BhcJ(J+1)/kT}. \tag{35.1}$$

This expression can be rearranged, thus,

$$Q_r = e^{Bhc/4kT} \sum_{J=0}^{J=\infty} 2(J + \tfrac{1}{2})e^{-Bhc(J+1/2)^2/kT},$$

and writing m for $(J + \tfrac{1}{2})$ we obtain

$$Q_r e^{-Bhc/4kT} = \sum_{m=1/2}^{m=\infty} 2m e^{-Bhcm^2/kT}. \tag{35.2}$$

This expression can be rewritten in the form

$$Q_r e^{-Bhc/4kT} = \sum_{m=1/2}^{m=\infty} 2m e^{-Bhcm^2/kT} - \sum_{m=1}^{m=\infty} 2m e^{-Bhcm^2/kT}, \tag{35.3}$$

[1] Mulholland, *Proc. Camb. Phil. Soc.*, **24**, 280 (1928).

where in the first sum m takes on all the values $\frac{1}{2}$, 1, $\frac{3}{2}$, 2, $\frac{5}{2}$, $\cdots$, $n/2$, $(n + 1)/2$, $\cdots$, ∞, and in the second sum the values 1, 2, 3, $\cdots$, $2n/2$, $\cdots$, ∞.

We now make use of the Euler-Maclaurin expansion formula in the form

$$\int_a^{a+r\omega} F(x)dx = \omega \left\{ \frac{1}{2}F(a) + F(a + \omega) + F(a + 2\omega) + \cdots + \frac{1}{2}F(a + r\omega) \right.$$
$$\left. + \sum_{m=1}^{n-1} \frac{(-)^m B_m \omega^{2m}}{(2m)!} F^{(2m-1)}(a + r\omega) - F^{(2m-1)}(a) \right\} + R_n, \quad (35.4)$$

where $F^{(2m-1)}$ indicates the $(2m - 1)$th derivative of F and $R_n = O(\omega^{2n})$. The quantities B_m are the Bernoulli numbers, $B_1 = \frac{1}{6}$, $B_2 = \frac{1}{30}$, $B_3 = \frac{1}{42}$, $B_4 = \frac{1}{30}$, $B_5 = \frac{5}{66}$ etc.[1] It is easily seen that both of the sums in (35.3) can be treated alike, in the first $\omega = \frac{1}{2}$ and in the second $\omega = 1$. In both

$$F(m) = 2me^{-Bhcm^2/kT} \tag{35.5}$$

and

$$F(0) = F(\infty) = 0;$$

thus, in place of equation (35.3) the following is obtained

$$Q_r e^{-Bhc/4kT} = \frac{2}{2}\{\frac{1}{2}F(0) + F(\frac{1}{2}) + F(\frac{1}{2} + \frac{1}{2}) + F(\frac{1}{2} + \frac{2}{2})$$
$$+ F(\frac{1}{2} + \frac{3}{2}) + \cdots F(\frac{1}{2} + 2\mu/2) + \cdots + \frac{1}{2}F(\frac{1}{2} + \infty/2)\}$$
$$- \{\frac{1}{2}F(0) + F(1) + F(1 + 1) + F(1 + 2) + F(1 + 3)$$
$$+ \cdots + F(1 + \mu) + \cdots + \frac{1}{2}F(1 + \infty)\}, \quad (35.6)$$

where μ is a typical integer. Applying (35.4) to each of the sums in (35.6) with $\omega = \frac{1}{2}$ in the first of them and $\omega = 1$ in the second

$$Q_r e^{-Bhc/4kT} = 2 \int_0^\infty 2xe^{-Bhcx^2/kT}dx - \int_0^\infty 2xe^{-Bhcx^2/kT} \qquad .$$
$$- 2 \sum_{n=0}^k \frac{(-)^{n+1}B_{n+1}(\frac{1}{2})^{2(n+1)}}{2(n+1)!} \{F^{(2n+1)}(\infty) - F^{(2n+1)}(0)\}$$
$$+ \sum_{n=0}^k \frac{(-)^{n+1}B_{n+1}}{2(n+1)!} \{F^{(2n+1)}(\infty) - F^{(2n+1)}(0)\} - 2R'_{k+1} + R''_{k+1}. \quad (35.7)$$

Carrying out the integrations in (35.7)

$$Q_r e^{-Bhc/4kT} = kT/Bhc$$
$$+ \sum_{n=0}^k \frac{(-)^{n+1}B_{n+1}}{2(n+1)!} (1 - 2^{-2n-1})\{F^{(2n+1)}(\infty) - F^{(2n+1)}(0)\} + R_{k+1}. \quad (35.8)$$

Because of the negative exponent, $F^{(2n+1)}(\infty)$ always vanishes. Also $F(0) = 0$, $F^I(0) = +2$, $F^{II}(0) = F^{IV}(0) = F^{VI}(0) = 0$, $F^{III}(0) = -4 \times 3(Bhc/kT)$, $F^V(0) = +6 \times 5 \times 4(Bhc/kT)^2$, $F^{VII} = -8 \times 7 \times 6 \times 5(Bhc/kT)^3$.

[1] See Whittaker and Watson, A Course of Modern Analysis (Fourth Edition), Cambridge University Press (1935), page 128.

Thus,

$$-\frac{(-)^{n+1}F^{(2n+1)}(0)}{2(n+1)!} = +\frac{(Bhc/kT)^n}{(n+1)!}$$

and

$$Q_r e^{-Bhc/4kT} = \frac{kT}{Bhc} + \sum_{n=0}^{k} \frac{B_{n+1}(Bhc/kT)^n}{(n+1)!}(1 - 2^{-2n-1}) + R_{k+1}, \quad (35.9)$$

$$Q_r e^{-Bhc/4kT} = kT/Bhc + \tfrac{1}{12} + \cdots + \text{etc.} \quad (35.10)$$

This is Mulholland's result. In the case of homonuclear molecules Q_r thus obtained must be divided by two because symmetry requirements for the wave functions only allow even or odd values of J. This statement also applies to the results obtained in the next three sections.

The energy of a $^1\Sigma$ diatomic molecule can be expressed by

$$\epsilon = (B_v)_e J(J+1) + (D_v)_e J^2(J+1)^2 + (F_v)_e J^3(J+1)^3 \\ + (v + \tfrac{1}{2})\omega_e + (v + \tfrac{1}{2})^2 x_e \omega_e + (v + \tfrac{1}{2})^3 y_e \omega_e + \epsilon_e, \quad (35.11)$$

where J takes on the values 0, 1, 2, 3, etc. and v the values 0, 1, 2, 3, etc.; the quantity ϵ_e is the electronic energy. For such a case the general expression for the partition function, due to the internal (including rotational degrees of freedom) is

$$Q_{\text{int.}} = \sum_e \sum_v \sum_J (2J + 1)e^{-\epsilon hc/kT}. \quad (35.12)$$

This expression can be written as

$$Q_{\text{int.}} = \sum_e \sum_v (Q_r)_{v,e} e^{-\epsilon_{ve}hc/kT}, \quad (35.13)$$

where

$$(Q_r)_{v,e} = \sum_J (2J + 1)e^{-\epsilon_{Jv}hc/kT} \quad (35.14)$$

and

$$\epsilon_{ve} = (v + \tfrac{1}{2})\omega_e + (v + \tfrac{1}{2})^2 x_e \omega_e + (v + \tfrac{1}{2})^3 y_e \omega_e + \epsilon_e, \quad (35.15)$$

$$\epsilon_{Jv} = B_{ve}J(J+1) + D_{ve}J^2(J+1)^2 + F_{ve}J^3(J+1)^3. \quad (35.16)$$

It is to be noted that the energies of electronic levels as obtained directly from experiment are

$$\epsilon_{0e} = \tfrac{1}{2}\omega_e + (\tfrac{1}{2})^2 x_e \omega_e + (\tfrac{1}{2})^3 y_e \omega_e + \epsilon_e,$$

i.e., they include the zero point vibrational energy obtained by putting $v = 0$ in the expression for the vibrational energy. However, as usually defined ϵ_e is the *electronic energy*. Evidently the replacement of $(Q_r)_{v,e}$ by an expression such as (35.10) will save tremendous labor in the evaluation of Q. If the molecule were completely rigid the expression given in (35.10) would suffice. Giauque and Overstreet solved this problem for the nonrigid case.

(36) **The Method of Giauque and Overstreet for Evaluating the Partition Function of $^1\Sigma$ Diatomic Molecules:**[1] In the following the subscripts v and e are dropped for convenience and ϵ_0' is written for $(\tfrac{1}{4})B + (\tfrac{1}{4})^2 D + (\tfrac{1}{4})^3 F$.* For a molecule with a $^1\Sigma$ ground state

$$Q_r = e^{hc\epsilon_0'/kT}\sum 2me^{[-hc(Bm^2+Dm^4+Fm^6+\cdots)]/kT}$$
$$= e^{hc\epsilon_0'/kT}\sum 2me^{-Bhcm^2/kT}e^{-Dhcm^4/kT}e^{-Fhcm^6/kT}, \quad (36.1)$$

where m has been written for $(J + \tfrac{1}{2})$. Expanding the second two exponential factors

$$Q_r = e^{hc\epsilon_0'/kT}\sum 2me^{-Bhcm^2/kT}\left[1 - \frac{Dhcm^4}{kT} + \frac{1}{2!}\left(\frac{Dhcm^4}{kT}\right)^2 + \cdots\right]$$
$$\times\left[1 - \frac{Fhcm^6}{kT} + \frac{1}{2!}\left(\frac{Fhcm^6}{kT}\right)^2 + \cdots\right], \quad (36.2)$$
$$= e^{hc\epsilon_0'/kT}\sum 2me^{-Bhcm^2/kT}\left[1 - \frac{Dhcm^4}{kT} - \frac{Fhcm^6}{kT} + \frac{1}{2!}\left(\frac{Dhcm^4}{kT}\right)^2\right.$$
$$\left. + \frac{Dhcm^4}{kT}\frac{Fhcm^6}{kT} + \frac{1}{2!}\left(\frac{Fhcm^6}{kT}\right)^2 + \cdots\right]. \quad (36.3)$$

Multiplying each term in the square brackets by the factor outside and considering the term by term sums, it is noted that the first sum is simply that whose value is given by (35.10). The remainder of the sums can be replaced by integrals of the form

$$I = \text{const.}\left(\frac{hc}{kT}\right)^r\int_0^\infty 2m^{2k+1}e^{-Bhcm^2/kT}dm$$
$$= \text{const.}\left(\frac{hc}{kT}\right)^r\frac{k!}{B^{k+1}}\left(\frac{kT}{hc}\right)^{k+1} \quad (36.4)$$

without loss of accuracy, e.g.,

$$\sum 2m^5e^{-Bhcm^2/kT} = \int_0^\infty 2m^5e^{-Bhcm^2/kT}dm + \frac{31}{4032}$$
$$= \frac{2!}{B^3}\left(\frac{kT}{hc}\right)^3 + \frac{31}{4032}. \quad (36.5)$$

Hence,

$$Q_r = e^{hc\epsilon_0'/kT}\frac{kT}{Bhc}\left[1 + \frac{B}{12}\cdot\frac{hc}{kT} - 2!\frac{D}{B^2}\left(\frac{kT}{hc}\right) - 3!\frac{F}{B^3}\left(\frac{kT}{hc}\right)^2\right.$$
$$\left. + \frac{4!}{2!}\cdot\frac{D^2}{B^4}\left(\frac{kT}{hc}\right)^2 + 5!\frac{DF}{B^5}\left(\frac{kT}{hc}\right)^3\right]. \quad (36.6)$$

---

[1] Giauque and Overstreet, *J. Am. Chem. Soc.*, **54**, 1731 (1932).

* Giauque and Overstreet use ϵ_0 for this quantity. Since for consistency the symbol ϵ_0 is used later in another connection we have used ϵ_0' instead.

This expression is in a form suitable for obtaining its first and second temperature derivatives.

An example of the results obtained is given in Table VI which shows the computation of Q_r for the lowest vibrational and electronic state of hydrogen chloride at $1000°$ K and $2000°$ K. The last column gives the value obtained by direct summing and the preceding one that obtained using equation (36.6).

TABLE VI

Comparison of Q_r Values for $H^{35}Cl$ by Summation and Approximation Methods

T	$e^{hc\epsilon_0'/kT} \times \dfrac{kT}{Bhc} \times \left(1 + \dfrac{Bhc}{12kT} - 2! \dfrac{D}{B^2} \cdot \dfrac{kT}{hc} - \cdots\right)$	Q Approx. $n = \frac{1}{2}$	$Q\Sigma$ $n = \frac{1}{2}$
$1000°$ K	$1.00374 \times 66.825 \times (1 + 0.00125 + 0.00684)$	67.618	67.618
$2000°$ K	$1.00184 \times 133.651 \times (1 + 0.00062 + 0.01386)$	135.84	135.85

The term $Bhc/12kT$ in the second column shows the effect of replacing the most important sum by an integral without correction. It is 0.125 per cent in Q_r at $1000°$ K and incidentally about 0.4 per cent in Q_r at $300°$ K. This would affect the free energy by 0.01 cal./mole at $300°$ K. The next term in this column shows that neglect of stretching at $1000°$ K would cause about five times the error produced by replacing the important sum by an integral, or about 0.02 cal./mole in the free energy at $1000°$ K.

Even after evaluating Q_r there is still considerable labor involved in determining the sum over the vibrational states as indicated in equation (35.13). Johnston and Davis [1] have found that at any temperature the value of $Q_{v,e} = (Q_r)_{v,e}e^{-(\epsilon_{ve}-\epsilon_{0e})}$ for any vibrational state bears a constant ratio to that for the next vibrational state. Thus only the quantities for the first few vibrational states need to be evaluated. In obtaining the temperature derivatives of Q, the quantities

$$d[(Q_r)_{v,e}e^{-(\epsilon_{ve}-\epsilon_{0e})}]/dT \quad \text{and} \quad d^2[(Q_r)_{v,e}e^{-(\epsilon_{ve}-\epsilon_{0e})}]/dT^2$$

appear: for these also the ratio of the value of the derivative in one vibrational state to that in the next is a constant; hence, only the values for first few vibrational states are needed.

All of the above expressions need to be modified for molecules whose ground state is not $^1\Sigma$ due to fact that p, the number of degenerate states, is no longer $2m = 2J + 1$ and the rotational energy is not of the form (35.16).

(37) **The Method of Gordon and Barnes [2] for Evaluating the Partition Function of $^1\Sigma$ Diatomic Molecules:** We shall modify the nomenclature and

---

[1] *J. Am. Chem. Soc.*, **56**, 271 (1934). These authors use $Q_v = (Q_r)_{v,e}e^{-(\epsilon_{ve}-\epsilon_{0e})}$ rather than the $(Q_r)_{e,e}$. The nomenclature used in this section is a compromise, made after a very helpful discussion with Professor H. L. Johnston.

[2] Gordon and Barnes, *J. Chem. Phys.*, **1**, 297 (1933).

equations of Gordon and Barnes to agree with the previous symbols used. For convenience we shall drop all the subscripts e, take $\epsilon_e = 0$ and introduce

$$q_v = kT/B_v hc, \tag{37.1}$$

$$d_v = (-2D_v/B_v)q_v, \tag{37.2}$$

$$f_v = (-6F_v/B_v)q_v^2. \tag{37.3}$$

We note that the last two terms in $\epsilon'_{0v} = \frac{1}{4}B_v + (\frac{1}{4})^2 D_v + (\frac{1}{4})^3 F_v$ are negligible and that $B_v/4$ can be replaced by $B_0/4$ in $e^{B_v hc/4kT}$ owing to the smallness of the terms it multiplies when the difference is appreciable. The quantity B_v can be expressed in the form

$$B_v = B_0/(1 + \beta_1 v + \beta_2 v^2), \tag{37.4}$$

thus

$$q_v = q_0(1 + \beta_1 v + \beta_2 v^2). \tag{37.5}$$

Since d_v and f_v only appear as correction terms in equation (36.6) it is sufficiently accurate to replace d_v and f_v by d_0 and f_0 respectively and also to replace q_v by q_0 in the correction terms. Thus equation (36.6) becomes

$$(Q_r)_v = e^{hc\epsilon_0', v/kT}q_0(1 + \beta_1 v + \beta_2 v^2)[1 + \frac{1}{12}q_0 + d_0 + 3d_0^2 + f_0] \tag{37.6}$$

or

$$(Q_r)_v = e^{1/4q_0}q_0(1 + \beta_1 v + \beta_2 v^2 + \frac{1}{12}q_0 + d_0 + 3d_0^2 + f_0 + \cdots). \tag{37.7}$$

In order to represent the partition function $Q'_{\text{int.}} = \sum (Q_r)_v c^{-hc(\epsilon_v - \epsilon_0)/kT}$ concisely we write

$$Q_v = \sum_v e^{-\epsilon_v hc/kT}, \quad \bar{v} = (\sum_v v e^{-\epsilon_v hc/kT})/Q_v \quad \text{and} \quad \bar{v}^2 = \sum_v v^2 e^{-\epsilon_v hc/kT}/Q_v. \tag{37.8}$$

Thus we obtain

$$Q'_{\text{int.}} = e^{1/4q_0}q_0 e^{\epsilon_0 hc/kT}Q_v(1 + \beta_1\bar{v} + \beta_2\bar{v}^2 + \frac{1}{12}q_0 + d_0 + 3d_0^2 + f_0), \tag{37.9}$$

where ϵ_0 stands for the zero point vibrational energy (i.e., that when $v = 0$ and $J = 0$). In taking the logarithm of $Q'_{\text{int.}}$ all the other terms in the last factor are small compared to the first (unity), and so we can conveniently expand this term in series and neglect all beyond the third term. Only the quantity due to d_0, namely $-\frac{1}{2}d_0^2$, need be counted from the third term of the expansion. Thus

$$\ln Q'_{\text{int.}} = (\ln Q_v + \epsilon_0 hc/kT) + \frac{1}{4}q_0 + \ln q_0 + \beta_1\bar{v} + \beta_2\bar{v}^2 + \frac{1}{12}q_0$$
$$+ d_0 + \frac{5}{2}d_0^2 + f_0. \tag{37.10}$$

Gordon and Barnes give tables for obtaining $(\ln Q_v + \epsilon_0 hc/kT)$, $\bar{v}$ and $\bar{v}^2$. Using (31.8) for the rotational and vibrational entropy we have

$$S_{r+v}/R = S_v/R + 1 + \ln q_0 + \beta_1 s_1 + \beta_2 s_2 + 2d_0 + 15d_0^2/2 + 3f_0, \tag{37.11}$$

where

$$S_v/R = \ln Q_v + T\partial \ln Q_v/\partial T \tag{37.12}$$

and

$$s_1 = \bar{v} + T\partial\bar{v}/\partial T; \quad s_2 = \bar{v}^2 + T\partial\bar{v}^2/\partial T^2. \tag{37.13}$$

Referring to (31.8), we can write for the heat capacity

$$C = T\partial S/\partial T = RT(2d \ln Q/dT + Td^2 \ln Q/dT^2). \tag{37.14}$$

For the rotational and vibrational heat capacity we have

$$C_{r+v}/R = C_v/R + 1 + \beta_1 c_1 + \beta_2 c_2 + 2d_0 + 15d_0^2 + 6f_0, \tag{37.15}$$

where

$$C_v/R = T\partial(S_v/R)/\partial T \tag{37.16}$$

and

$$c_1 = T\partial s_1/\partial T; \quad c_2 = T\partial s_2/\partial T. \tag{37.17}$$

Gordon and Barnes give tables for obtaining S_v/R, C_v/R, s_1, s_2, c_1 and c_2.

The accuracy of this method at higher temperatures suffers partly owing to neglect of higher terms in (36.3) and also to the use of q_0 for q_v in the correction terms. It never suffers from replacement of sums by uncorrected integrals in the correction terms. This might be true below room temperatures, but then the ordinary summation method is often more convenient. Kassel has developed expressions where none of the above approximations are made.

(38) **The Method of Kassel for Evaluating the Partition Function of $^1\Sigma$ Diatomic Molecules:** Kassel[1] obtains $(Q_r)_v$ in the same way as Giauque and Overstreet except that he does not assume that sums can be replaced by integrals even in correction terms. He gives the necessary correction terms to these integrals in his paper.

The final result obtained (dropping the subscript v) is

$$Q_r = \frac{kT}{hcB} + \frac{1}{3} + \frac{1}{315} \cdot \frac{hc}{kT}(21B - 8D - 6F) + \cdots - 2\frac{D}{B}\left(\frac{kT}{hcB}\right)^2$$

$$+ \left[12\left(\frac{D}{B}\right)^2 - 6\left(\frac{F}{B}\right)\right]\left(\frac{kT}{hcB}\right)^3 + \cdots. \tag{38.1}$$

This result corresponds to (36.6) and is identical with it except for the fact that the correction terms were not neglected when replacing sums by integrals in the smaller terms. The term $hc\epsilon_0'/kT$ in (36.6) has been expanded in series and multiplied out.

The importance of Kassel's contribution consists in his method of evaluating

$$Q'_{\text{int.}} = \sum (Q_r)_v e^{-(\epsilon_v - \epsilon_0)/kT}. \tag{38.2}$$

[1] *J. Chem. Phys.*, **1**, 576 (1933); *Chem. Rev.*, **18**, 277 (1936).

First of all $(Q_r)_v$ is expressed as a power series in v by substituting

$$\left.\begin{array}{l} B_v = B_0 + \alpha v + \beta v^2, \\ D_v = D_0 + \gamma v + \delta v^2, \end{array}\right\} \tag{38.3}$$

multiplying out and rearranging. In equation (38.3), $\alpha = -B_0\beta_1$ and $\beta = -B_0\beta_2$ is the connection between Kassel's and the Gordon and Barnes constants. The next step is to express

$$(Q_r)_v e^{[-(v+1/2)^2 x_e \omega_e - (v+1/2)^3 y_e \omega_e]/kT}$$

as a power series $p(v)$ in v by expanding the exponential and multiplying out. Thus,

$$p(v) = \sum \epsilon_n v^n;$$

then

$$Q'_{\text{int.}} = \sum_0^\infty p(v) e^{-(v+1/2)\omega_e/kT} = (1-z)^{-1} \sum f_n g_n,$$

where

$$z = e^{-(v+1/2)\omega_e/kT}; \quad f_n = (1-z) \sum_{v=0} v^n z^v.$$

The important values of f_n are

$$f_0 = 1$$
$$f_1 = z(1-z)^{-1}$$
$$f_2 = z(1+z)(1-z)^{-2}$$
$$f_3 = z(1+4z+z^2)(1-z)^{-3}$$
$$f_4 = z(1+11z+11z^2+z^3)(1-z)^{-4}$$
$$f_5 = z(1+26z+66z^2+26z^3+z^4)(1-z)^{-5}$$
$$f_6 = z(1+57z+302z^2+302z^3+57z^4+z^5)(1-z)^{-6}$$
$$f_7 = z(1+120z+1191z^2+2416z^3+1191z^4+120z^5+z^6)(1-z)^{-7}$$
$$f_8 = z(1+247z+4293z^2+15619z^3+15619z^4+4293z^5+247z^6+z^7)(1-z)^{-8}.$$

This method is more accurate but more complicated than that of Gordon and Barnes.

(39) **Evaluation of the Partition Function of Other Types of Diatomic Molecules and Polyatomic Molecules:** The general manner in which these methods can be extended to types of diatomic molecules, other than $^1\Sigma$, is more or less obvious; it has been discussed by Kassel.[1] The application to polyatomic molecules has also been described by Kassel and by Gordon.[2] The respective methods used by Kassel and by Gordon are analogous to their

[1] *Loc. cit.*
[2] *J. Chem. Phys.,* **2**, 65, 549 (1934); **3**, 259 (1935).

methods for $^1\Sigma$ diatomic molecules. Both procedures start with the equation

$$Q_{\text{int.}} = \sum_{v_1} \sum_{v_2} \cdots \sum_{v_k} (Q_r)_{v_1, v_2, \cdots, v_k} e^{-\epsilon_{v_1, v_2, \cdots, v_k}/kT}, \tag{39.1}$$

where $Q_{\text{int.}}$ refers to all degrees of freedom except translation and those of nuclear spin and where $\epsilon_{v_1, v_2, \cdots, v_k}$ is the vibrational energy defined by the quantum numbers $v_1, v_2, \ldots, v_k$ and the rotational partition function $(Q_r)_{v_1, v_2, \cdots v_k}$ depends on all the quantum numbers.

(40) **The Separation of Rotational and Vibrational Partition Functions:** The methods given in the previous paragraphs have shown that

$$Q_{\text{int.}} = \sum_i (Q_r)_i e^{-\epsilon_i/kT}, \tag{40.1}$$

where i stands for all vibrational quantum numbers. It can be assumed without great loss of accuracy (a few hundredths of a calorie per degree per mole),[1] that $(Q_r)_i$ has the same value, Q_r, for all vibrational states, thus

$$Q_{\text{int.}} = Q_r \sum e^{-\epsilon_i/kT}, \tag{40.2}$$

$$= Q_r Q_v, \tag{40.2}$$

where Q_v is known as the vibrational partition function

$$Q_v = \sum_i e^{-\epsilon_i/kT}.$$

The vibrational energy is approximately the sum of the energies due to each mode of vibration and thus

$$Q_v = \sum_{v_1} \sum_{v_2} \cdots \sum_{v_k} e^{-\epsilon_{v_1}/kT} e^{-\epsilon_{v_2}/kT} \cdots e^{-\epsilon_{v_k}/kT}, \tag{40.3}$$

where ϵ_{v_k} is the energy of the kth mode of vibration determined by the quantum number v_k

$$Q_v = (q_v)_1 (q_v)_2 \cdots (q_v)_k,*$$

where

$$(q_v)_k = \sum_{v_k} e^{-\epsilon_{v_k}/kT} \tag{40.4}$$

is the vibrational partition function associated with the kth mode of vibration. The evaluation of this quantity is considered in Section (42).

The energy, heat capacity, and entropy are all functions of $\log Q$ and its derivatives. Thus these quantities for the rotational and vibrational degrees of freedom can be split up into a part due to rotation, and parts due to each vibrational mode just as the translational part was previously separated.

(41) **The Partition Function for Classical Rotation of Rigid Molecules:** The methods of Sections (35) to (39) can be used to calculate the partition

---

[1] Wilson, *ibid.*, **7**, 948 (1939).

* The roman symbol q_v is used to avoid confusion with q_v defined by (37.1).

function for diatomic and rigid polyatomic molecules at high temperatures, i.e., in the classical limit. Except for hydrogen, the results hold even at room temperatures and for polyatomic molecules they hold down to below 90° K. The partition functions are as follows:

Diatomic Molecules

$$Q_r = \frac{8\pi^2 I k T}{h^2 \sigma} \tag{41.1}$$

results from (35.10) by omitting $e^{Bhc/4kT}$ and noting that the term $\frac{1}{12}$ is negligible.

Rigid Polyatomic Molecules

$$Q_r = \frac{8\pi^2 (8\pi^3 ABC)^{1/2} (kT)^{3/2}}{h^3 \sigma}, \tag{41.2}$$

where A, B, C are the moments of the molecule about *principal* axes through the center of gravity.[1] The factor σ in the denominator of equation (41.1) and (41.2) arises because the results came from integrals which replace sums over *all* quantum states. Actually only quantum states are allowed whose wave functions are *either* symmetrical *or* antisymmetrical in the nuclei. This restriction reduces the number of states by a quantity σ, which is equal to two for homonuclear diatomic molecules and unity for heteronuclear. For polyatomic molecules it is the number of equivalent positions of the molecule that can be produced by rotation about axes of symmetry in the molecule.[2] By substituting (41.1) and (41.2) into equation (34.7) the values RT and $3RT/2$ respectively are obtained for the rotational energies of classically excited diatomic and rigid polyatomic gases. Similarly substituting in (34.8) gives R and $3R/2$ for the respective rotational heat capacities in agreement with the principle of equipartition. Generally it is not convenient to choose principal axes; however, if any three axes at right angles (X, Y, Z) are chosen through the center of gravity of the molecule about which the moments of inertia are $A' = \sum_i m_i(y_i^2 + z_i^2)$, $B' = \sum_i m_i(z_i^2 + x_i^2)$ and $C' = \sum_i m_i(x_i^2 + y_i^2)$, while the products of inertia are $\{xy\} = \sum m_i x_i y_i$, $\{yz\} = \sum m_i y_i z_i$, $\{xz\} = \sum m_i x_i y_i$ (where m_i, x_i, y_i, and z_i are respectively the mass and coordinates of the ith atom)

$$ABC = \begin{vmatrix} A' & -\{xy\} & -\{xz\} \\ -\{xy\} & B' & -\{yz\} \\ -\{xz\} & -\{yz\} & C' \end{vmatrix}, \tag{41.3}$$

[1] Kassel, *Chem. Rev.*, **18**, 277 (1936).
[2] Mayer, Brunauer, and Mayer, *J. Am. Chem. Soc.*, **55**, 37 (1933).

where the right-hand number is the determinant of the nine quantities involved. Equation (41.3) follows from the theory of quadratic forms but it is instructive to note that when X, Y and Z become the principal axes the products of inertia vanish by definition and equation (41.3) reduces to the identity

$$ABC = \begin{vmatrix} A & 0 & 0 \\ 0 & B & 0 \\ 0 & 0 & C \end{vmatrix}. \tag{41.4}$$

It is to be noted that, in both cases, a factor $e^{\epsilon_0'/kT}$ has been omitted from Q_r where ϵ_0' is the quantity or one analogous to that appearing in Section (36). The omission is made because while it affects the absolute energy as given by equation (34.7) by subtracting the constant term $N\epsilon_0'$, it does not affect the heat capacity and entropy as given by (34.8) and (31.11). This is because it disappears by logarithmic differentiation in the former, and cancels between the two terms in the latter. Looked at another way, the energy zero is shifted by $(-\epsilon_0')$. Both (41.1) and (41.2) are special cases of an equation to be derived later which also considers free internal rotation.

(42) **The Vibrational Partition Function:** In general the vibrational energy of a molecule lies in several degrees of freedom each of which constitutes a mode of vibration. Such modes of vibration are often called "Einstein modes."[1] The energy for a particular quantum state is approximately

$$\epsilon_v = (v + \tfrac{1}{2})h\nu_0, \tag{42.1}$$

where $v = 1, 2, 3, 4$, etc.[2]

The partition function is

$$q_v = e^{-h\nu_0/2kT} \sum e^{-vh\nu_0/kT} \tag{42.2}$$

or

$$q_v = e^{-h\nu_0/2kT} \sum e^{-vx}, \tag{42.3}$$

where $x = h\nu_0/kT$.

By the binomial theorem, since $e^{-vx} < 1$,

$$\frac{1}{1 - e^{-x}} = \sum e^{-vx}, \tag{42.4}$$

so that

$$q_v = \frac{e^{-h\nu_0/2kT}}{1 - e^{-x}}. \tag{42.5}$$

[1] Einstein, *Ann. Physik*, **22**, 180 (1907).

[2] Each degree of freedom is associated with a normal coordinate whose time rate of change corresponds to that of a harmonic oscillator, of this frequency. Whether any mode will produce absorption of light in the infra-red or a Raman shift of frequency ν depends on the symmetry of the vibration. For an excellent discussion of this subject see Kohlrausch, Der Smekal-Raman-Effekt, Ergänzungsband (1931–1937), Julius Springer, Berlin, pages 1–76.

For the same reason that $e^{\epsilon_0'/kT}$ could be omitted previously from the rotational partition function, we may now omit the factor $e^{-h\nu_0/2kT}$ from (42.5) and take

$$q_v = \frac{1}{1 - e^{-x}} = \frac{1}{1 - e^{-h\nu_0/kT}} \qquad (42.6)$$

as the vibrational partition function.

(43) **The Energy and Heat Capacity of Gases:** The rotational energy levels for a diatomic gas are given by

$$\epsilon = \frac{J(J + 1)h^2}{8\pi^2 I}, \qquad (43.1)$$

where I is the moment of inertia of the molecule and the quantum number J can take on the values 1, 2, 3, 4, etc. To each value of J and of ϵ there is another set of quantum numbers $M = 0, \pm 1, \pm 2, \cdots, \pm J$; each value of M corresponds to a different orientation of the plane of rotation of the molecule with respect to some arbitrary axis. There are $2J + 1$ orientations or quantum states corresponding to each value of J: thus, in equation (21.1) $p_i = 2J + 1$ and the partition function is

$$Q_r = \sum_J (2J + 1)e^{-J(J+1)h^2/8\pi^2 IkT}. \qquad (43.2)$$

The expressions for the molal rotational energy and heat capacity are obtained by substituting this expression in equations (34.7) and (34.9) respectively.

For all molecules except hydrogen, the use of these formulae gives RT and R for the molal rotational energy and heat capacity respectively at temperatures above 70° K. This is because, except for hydrogen, the moment I is sufficiently large to reduce the exponent of the terms for the higher energy states in the sums. Hence, there are relatively large numbers of molecules in the higher energy states, a situation which we have already seen approximates closely to the classical case, and therefore yields the equipartition values of the energy and heat capacity.

In the case of hydrogen this procedure yields calculated values for the rotational energy and heat capacity that are less than the equipartition values even at room temperature. This result is in general agreement with experiment. The solid curve in Fig. 4 is a graph of C_r/R calculated using equation (43.2) with the moment of inertia I chosen to give the best fit with the experimental data. This value should at first sight be equal to C_v^0 (value corrected to ideal state) for hydrogen, minus $\frac{3}{2}R$ (the translational heat capacity) since the vibrational heat capacity is negligible. The designated points on Fig. 4, which give the experimental values of $C_r/R = (C_v^0 - \frac{3}{2}R)/R$, certainly are not in agreement with the equation.

Ordinary hydrogen consists of two varieties, para and ortho. In the para-hydrogen the spins of the nuclei are opposed ($S = \frac{1}{2} - \frac{1}{2} = 0$) giving an

antisymmetrical wave function. Thus, in order to keep the total wave function antisymmetrical in the nuclei, only the even rotational levels with $J = 0, 2, 4, 6, 8$, etc., which are symmetrical in the nuclei, are allowed. On the other hand, in ortho-hydrogen the spins have the same sign and the spin quantum number is unity ($S = \frac{1}{2} + \frac{1}{2} = 1$). This, however, allows three possible orientations ($p = 2S + 1 = 3$) of the spin, all of which have symmetrical wave functions. For each of these orientations only the rotational levels, $J = 1, 3, 5, 7, 9$, etc., are allowed in order to make the total wave function
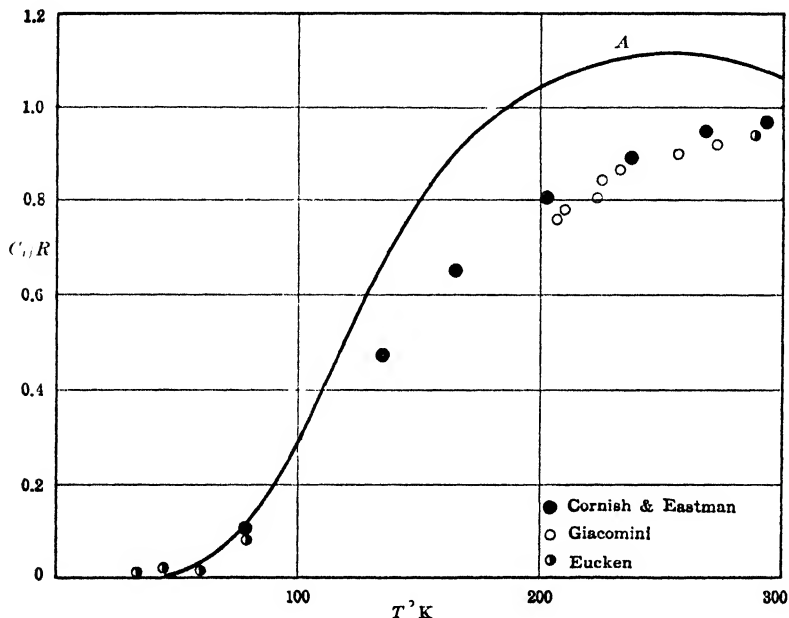
FIG. 4.* The Heat Capacity C_r/R of a Rigid Rotor

antisymmetrical in the nuclei. All three orientations can go with the same rotational levels and so they yield the same properties and are physically indistinguishable parts of ortho-hydrogen but distinguishable from para-hydrogen. Since ordinary hydrogen is formed under ordinary conditions, which are practically classical, the para and ortho states are found in the ratio 1 : 3 due to the three varieties of the latter. The heat capacity of ordinary hydrogen must, therefore, be calculated on the basis that hydrogen is composed of two substances which cannot change into each other in the time of an experiment.

* (a) Cornish and Eastman, *J. Am. Chem. Soc.*, **50**, 627 (1928). (b) Giacomini, *Phil. Mag.*, **50**, 146 (1925). (c) Eucken, *Verh. d. Phys. Ges.*, **18**, 4 (1916). (d) Curve A—Dieke, *Physica*, **5**, 412 (1925).

The partition function for para-hydrogen is

$$(Q_r)_{\text{para}} = \sum_{J=0,2,\text{etc.}} (2J+1)e^{-J(J+1)h^2/8\pi^2IkT}, \tag{43.3}$$

while that for ortho-hydrogen is

$$(Q_r)_{\text{ortho}} = \sum_{J=1,3,\text{etc.}} (2J+1)e^{-J(J+1)h^2/8\pi^2IkT}. \tag{43.4}$$

The rotational heat capacity of para-hydrogen is thus, according to (34.8),

$$(C_r)_{\text{para}} = \frac{R}{T^2} \cdot \frac{\partial^2 \log (Q_r)_{\text{para}}}{\partial(1/T)^2}, \tag{43.5}$$

while that for ortho-hydrogen is

$$(C_r)_{\text{ortho}} = \frac{R}{T^2} \cdot \frac{\partial^2 \log (Q_r)_{\text{ortho}}}{\partial(1/T)^2}. \tag{43.6}$$

For ordinary hydrogen the rotational heat capacity is therefore

$$C_r = \tfrac{1}{4}(C_r)_{\text{para}} + \tfrac{3}{4}(C_r)_{\text{ortho}}.$$

To obtain the total heat capacity at constant volume for the ideal gas state the value thus obtained is increased by $\tfrac{3}{2}R$, of course. The curve in Fig. 5 shows the values of C_v^0 calculated for hydrogen at the several temperatures. It is in excellent agreement with the experimental data (corrected to the ideal gas state) which are also plotted. We shall have reason to return to this subject later in connection with the entropy of ordinary hydrogen.[1]

At high temperatures there are contributions to the energy and heat capacity due to the vibration (relative motion between the hydrogen atoms). To a first approximation these can be calculated using (43.7) and (43.8) and added to the rotational and translational energy and heat capacity. The frequency of vibration can be taken as the same in both the ortho and para forms.

In the case of gaseous hydrogen deuteride, which has heteronuclear molecules, all energy levels are allowed so that equation (43.2) summed over all values of J gives the correct partition function to use in calculating the heat capacity.

Gaseous deuterium presents essentially the same problem as gaseous hydrogen. In this case the nuclei have one unit of spin and the ortho-type molecules have even J values. Moreover the ortho-type form two-thirds of the high temperature equilibrium mixture and the para-type one-third.

While the translational degrees of freedom can always be separated, it is not always sufficiently accurate to separate the rotational and vibrational heat capacity as has been done above. The accurate procedure is to express the

[1] For an excellent discussion of this subject see Giauque, *J. Am. Chem. Soc.*, **52**, 4816 (1930).

energy levels as a function of the rotational and vibrational quantum numbers and set up the partition function (21.1) accordingly. The heat capacity is then calculated by equation (34.9). For most cases, except that of hydrogen below room temperature, one of the procedures outlined in Sections (36), (37), (38) and (39) can be used to evaluate the partition function. For hydrogen below room temperature the direct summation procedure is preferable. For the case of hydrogen it has been shown by Birge, Lyman and Jeppesen[1] from the band spectrum of hydrogen that the rotational and vibrational energy can be repre-
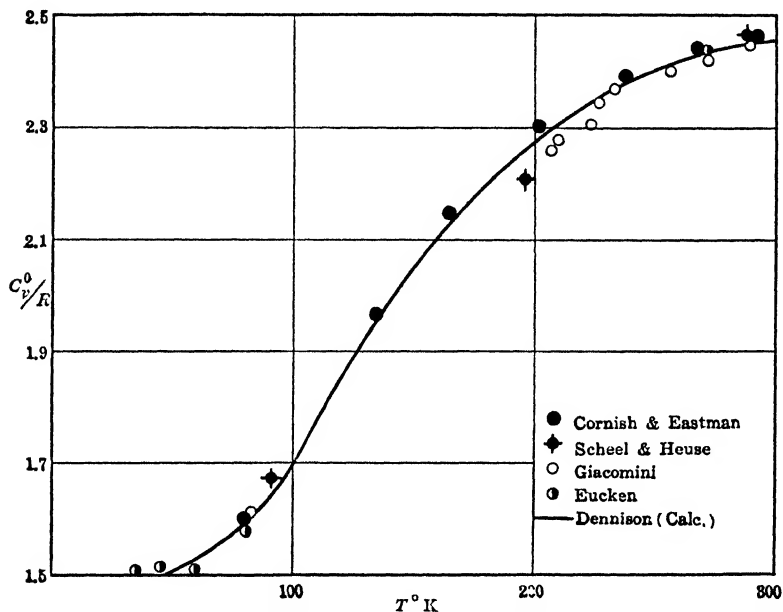
Fig. 5.* The Heat Capacity C_v^0/R of Hydrogen at Constant Volume in the Ideal Gas State

sented by an equation of the form (35.11). For para-hydrogen the partition function is given by equation (35.12) summed over the even values of J (including zero) while for ortho-hydrogen the sum is taken over the odd values of J using the same equation.

The procedure in calculating the heat capacity of ordinary hydrogen is then the same as above, except for the use of the exact partition function for rotation and vibration instead of the simple rotational one. The calculation has been carried out by Giauque.[2]

* (a) Cornish and Eastman, *J. Am. Chem. Soc.*, **50**, 627 (1928).   (b) Scheel and Heuse, *Ann. Physik*, **43**, 473 (1913).   (c) Giacomini, *Phil. Mag.*, **50**, 146 (1925).   (d) Eucken, *Verh. d. Phys. Ges.*, **18**, 4 (1916).   (e) Dennison, *Proc. Roy. Soc.*, [A], **115**, 483 (1927).

[1] See Giauque, *J. Am. Chem. Soc.*, **52**, 4816 (1930).

[2] *Loc. cit.*

By substituting equation (42.6) for the vibrational partition function into equation (34.7), the energy per mole associated with a single vibrational mode is

$$E - E_0 = \frac{RTx}{e^x - 1},\tag{43.7}$$

the zero-point energy level being taken as zero. By substitution into (34.8)

$$C = \frac{Rx^2 e^x}{(e^x - 1)^2},\tag{43.8}$$

where $x = h\nu_0/kT$ was substituted before differentiation in obtaining both (43.7) and (43.8).

Tables for $(E - E_0)/T$ from (43.7) and C from (43.8) are given in Appendix I. These are called "Einstein functions."[1] This treatment is valid whenever the rotational and vibrational partition functions are separable.

It is of interest to evaluate C at high temperatures. When T is large x is small and e^x can be replaced by the first two terms of its power expansion, namely $(1 + x)$; thus,

$$C = \frac{Rx^2(1 + x)}{x^2} = R(1 + x).\tag{43.9}$$

However, since x is small it can be neglected compared with unity so $C = R$, a result which has already been obtained from the *principle of equipartition*.

Methane has five atoms corresponding to fifteen degrees of freedom: the translation and rotation of the molecule account for six of these, leaving nine degrees of freedom, all of which are vibrational in character. The nine degrees of freedom, in this case, give rise to only four fundamental frequencies or modes of vibration. One of these (ν_1) corresponds to one of the degrees of freedom, a second $(\nu_{2,3})$ corresponds to two of the degrees of freedom while the remaining two $(\nu_{4,5,6}$ and $\nu_{7,8,9})$ each correspond to three degrees of freedom. The frequencies have the values: $\nu_1 = 2915$, $\nu_{2,3} = 1520$, $\nu_{4,5,6} = 1304$, $\nu_{7,8,9} = 3022$ cm.$^{-1}$.[2] Equation (43.8) is applied to *each* degree of freedom and all the values are added. To obtain the total heat capacity at constant pressure of the gas at low pressure (C_p^0), $6R/2$ must also be added for the translation and rotation, which are both classically excited, and R for $(C_p - C_v)$. If the heat capacity is required at higher pressures the value of $(C_p - C_v)$ must be obtained from the data of state, thus

$$C_p - C_v = R + T \int_0^P \left(\frac{\partial^2 V}{\partial T^2}\right)_p dP.$$

Values of C_p^0 for methane at various temperatures calculated by this method

---

[1] Einstein, *loc. cit.*

[2] For discussion see Kassel, *J. Am. Chem. Soc.*, **55**, 1357 (1933).

are shown by the curve in Fig. 6 in which circles are experimental points. A somewhat better agreement can be obtained if allowance is made for interaction of rotation and vibration.
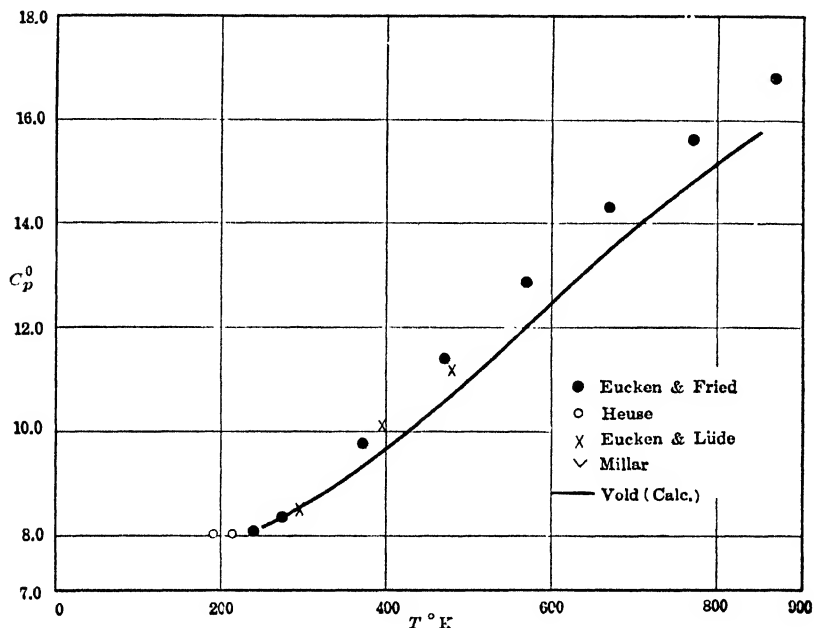
FIG. 6.* The Heat Capacity C_p^0 of Methane at Constant Pressure in the Ideal Gas State

(44) **The Entropy of Gases—Effect of Isotopic Composition**: The entropy of a gas is the sum of the translational entropy as given by equation (32.13) and the entropy due to other degrees of freedom as given by equation (32.18). These equations strictly should be applied to only one of the isotopic species present in a gas. The total entropy of the gas is then obtained by calculating the entropy of the gas due to each isotope and adding these together.

$$S' = \sum_i x_i S_i, \tag{44.1}$$

where x_i and S_i are respectively the mole fraction and entropy of each isotopic species. To the total S' must be added the entropy of mixing

$$\Delta S_m = - R \sum x_i \ln x_i. \tag{44.2}$$

* (a) Eucken and Fried, *Physik*, **29**, 41 (1924). (b) Heuse, *Ann. Physik*, **59**, 86 (1919). (c) Eucken and Lüde, *Z. phys. Chem.*, **B, 5**, 413 (1929). (d) Millar, *J. Am. Chem. Soc.*, **45**, 874 (1923). (e) Vold, *ibid.*, **57**, 1192 (1935).

Since the isotopic composition of compounds is normally constant the entropy of mixing as given by (44.2) is constant and is only manifest in processes involving the separation of isotopes. In the crystal the isotopic crystals form a perfect solution. It is therefore evident that the entropy of mixing may be left out of consideration except in processes involving the separation of isotopes.

Where homonuclear molecules are involved, the rotational and vibrational entropy of the symmetry varieties is essentially the same for all gases except hydrogen and deuterium. The practical entropy may therefore be computed for each isotopic species as described above. However, the sum in the rotation-vibrational partition function of equation (32.18) can be taken over energy levels which are averages of the levels of the isotopes, weighted according to composition. This gives an average value of the practical rotational and vibrational entropy of the isotopes and combined with a translational entropy, calculated from (32.13) using the average molecular weight, gives a result differing only minutely from that calculated using equation (44.1). The average over the energy levels can be obtained directly from averages taken over the spectroscopic multiplets weighted according to intensity. The computation of the entropy due to nuclear spin [1] is a complicated process, as, in general, the isotopes have different nuclear spins and symmetry requirements.

The translational entropy under all cases is given by the equation

$$S_t = R[\tfrac{5}{2} \ln T - \ln P + \tfrac{3}{2} \ln M + \ln p_s - 1.164], \qquad (44.3)$$

which is equation (32.13) with the numerical values of the constants substituted; P is the pressure in atmospheres and M is the weight per mole of the isotopic mixture. The quantity p_s which is the number of spin states of equal energy may be taken to include the nuclear spin if desired.

(45) **The Entropy of Hydrogen Chloride and of Oxygen:** As an example of the computation of the entropy by the method of direct sums where only a single electronic state is involved we shall compute the entropy of hydrogen chloride directly from the spectroscopic data.

At 298.15° K and 1 atm. pressure, the entropy of hydrogen chloride in the ideal gas state due to translation is obtained by substitution in equation (44.3) with p_s equal to unity and $M = 36.46$. This gives the result 36.715 cal. per degree per mole. To obtain a final value of the entropy it is necessary to add the entropy due to rotation and vibration as given by equation (31.7). To substitute in equation (31.7) one needs to know the energy levels due to rotation and vibration for the hydrogen chloride molecule. For these we shall take a weighted average of those for the two isotopes, using the data of Colby, Meyer and Bronk.[2] The energy levels for the first two vibrational states $v = 0$ and $v = 1$ are given by a formula like equation (35.11) with no electronic states above the ground one (i.e., $\epsilon_e = 0$). Column 1 gives the value of J; the values of the energy (in cm.$^{-1}$) are given in column 2 of Table VII. The latter were

[1] Giauque and Overstreet, *J. Am. Chem. Soc.*, **54**, 1731 (1932).

[2] *Astrophys. J.*, **50**, 251 (1919).

TABLE VII

CONTRIBUTION OF ENERGY STATES TO THE ENTROPY OF HYDROGEN CHLORIDE AT 298.15° K

J	cm.$^{-1}$	$p = 2J + 1$	$e^{-\epsilon/kT}$ $v = 0$	$pe^{-\epsilon/kT}$	$p\epsilon e^{-\epsilon/kT}$ cal. $\times 10^{15}$
0	0.0	1	1.0000	1.0000	0.00
1	20.9	3	0.9041	2.7123	11.26
2	62.8	5	0.7387	3.6935	46.95
3	125.7	7	0.5453	3.8171	95.27
4	209.3	9	0.3643	3.2787	136.27
5	313.3	11	0.2206	2.4266	150.96
6	438.9	13	0.1204	1.5652	136.40
7	584.1	15	0.0597	0.8955	103.86
8	750.6	17	0.0268	0.4556	67.90
9	937.5	19	0.0109	0.2071	38.55
10	1143.9	21	0.0040	0.0840	19.08
11	1372.0	23	0.0013	0.0299	8.15
12	1618.4	25	0.00041	0.0103	3.30
13	1886.1	27	0.00011	0.0030	1.12
14	2172.5	29	0.00003	0.0009	0.38
15	2451.3	31	0.00001	0.0003	0.12
				20.18	818.72

$v = 1$

J	cm.$^{-1}$	$p = 2J + 1$	$e^{-\epsilon/kT}$ $v = 0$	$pe^{-\epsilon/kT}$	$p\epsilon e^{-\epsilon/kT}$ cal. $\times 10^{15}$
0	2886.1	1	0.00000	0.0000	0.000
1	2906.5	3	0.00000	0.0000	0.000

obtained directly from the centers of the lines in the P and R branches of the $v = 0$ to $v = 1$ band. This band is shown schematically in the lower half of Fig. 7; the upper half of Fig. 7 shows the rotational energy levels for $v = 0$ and $v = 1$. Above each line is shown the transition which produces it. A line in the R branch corresponds to an increase of unity in J while one of the P branch represents a decrease of unity; in both cases v increases from zero to unity. Thus one can always find a line in the P branch and a line in the R branch that correspond to transitions ending in a common level. The first line $R1$ of the R branch ($\nu = 2906.5$ cm.$^{-1}$) corresponds to J going from zero to unity. The second line of the P branch, $P2(\nu = 2843.7$ cm.$^{-1})$ begins with $J = 2$ and ends with $J = 1$. The difference between these lines 62.8 cm.$^{-1}$ gives the energy of the level, $v = 0$, $J = 2$. The selection rules do not admit the transition $v = 0$, $J = 0$ to $v = 1$, $J = 0$ but a value for the missing line ($\nu = 2886.1$ cm.$^{-1}$) can be obtained by extrapolating the R branch. Subtracting from this the first line of the P branch, $P1(J = 1$ to $J = 0)$ ($\nu = 2865.2$ cm.$^{-1}$) an energy of 20.9 cm.$^{-1}$ is found for the level, $v = 0$, $J = 1$. In this way the rest of the rotational levels for $v = 0$ were obtained: the rotational levels for $v = 1$ can be derived in a similar manner. Pairs of lines in the P and R branches *beginning* in a common level are taken to obtain differences

between the rotational levels for $v = 1$. Finally these differences are combined with the energy of the $v = 0$, $J = 0$ to $v = 1$, $J = 0$ transition. To convert these energy levels from cm.$^{-1}$ to ergs requires multiplication by $hc = 1.9856 \times 10^{-16}$ where c is the velocity of light. Column 3 gives the value of p (the number of levels with energy ϵ differing only in orientation) while column 4 gives $e^{-\epsilon/kT}$. To obtain the exponent the energy in cm.$^{-1}$ is multiplied by
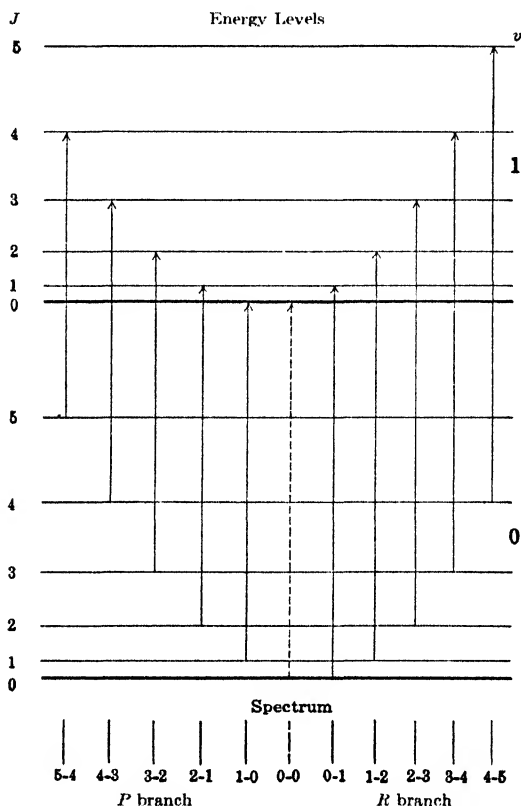
Fig. 7.   Energy Levels of Hydrogen Chloride (Schematic)

$hc/kT = 1.4383/T$.   In the fifth column the values of column four are multiplied by p and in the sixth they are multiplied by $p\epsilon$.   The sum of the values in column five gives Q; that of the values in column six gives the other sum involved in the calculation of the entropy.   These sums are substituted into equation (31.7) with the result

$$S = 1.9869 \left[\frac{10}{1.3805 \times 298.15} \left(\frac{818.7}{20.18} \right) + 2.303 \log 20.18 \right] = 7.928. \quad (45.1)$$

Combining this value with the translational entropy one obtains 44.643 cal. per degree per mole for the entropy of hydrogen chloride at 298.15° K and 1 atm. This calculation was first made correctly by Giauque and Wiebe,[1] using a thorough but more intricate interpretation of the infra-red data, but their result does not differ essentially from that given above. The procedure used here has been employed because it demonstrates clearly the relation of the final value to the spectroscopic lines.

As an illustration of the use of equation (31.7) in a rather complicated case we shall, very briefly, consider the entropy of oxygen. The paramagnetism of the oxygen molecule is due to two electrons with unpaired spins; the spin quantum number S is therefore unity. The angular momentum due to the spin of the electrons may be at right angles to the nuclear angular momentum and therefore the component of S in the direction of the nuclear angular momentum, with quantum number K, is zero; the two may be *parallel* in which case K and S are additive, or the two may be *antiparallel* in which case S subtracts unity from K. In this way, for a given value of K, three distinct energy levels are produced. If J represents the vector sum of K and S, these levels in order of decreasing energy have J values of $K + 1$, K and $K - 1$ which is the quantum number governing the total angular momentum vector. This vector has $2J + 1$ orientations with respect to an arbitrary field so that $2J + 1 = p$ levels of the same energy correspond to each value of J. The set of energy levels with $J = K + 1$ are called the F_1 levels while those with $J = K$ and $K - 1$ are called the F_2 and F_3 levels respectively. The energy of these levels is largely determined by K.[2] The F_2 rotational levels can be represented by a formula similar to (35.16) with K replacing J while the F_1 and F_2 levels lie closely on either side.

Because the nucleus of oxygen has an even number of protons, the wave function must be symmetrical in the nuclei (hydrogen and nitrogen have an *odd* number of protons in their nuclei). The symmetry requirements limit the values of K to 1, 3, 5, 7, 9, etc. The energy levels involved have been obtained from the data of Dieke and Babcock[3] and the entropy has been calculated by Giauque and Johnston.[4]

The entropy of oxygen is obtained by adding together the translational contribution as given by equation (44.3) and the contribution due to the electronic, vibrational and rotation energy levels as given by equation (31.7). The values of ϵ to be used in (31.7) are due to vibration and rotation together with the effect produced by the three relative orientations of the spin angular momentum, namely the three groups F_1, F_2 and F_3. The values of p have already been discussed. Table VIII gives the totals of the terms in the sums $pe^{-\epsilon/kT}$ and $k^{-1}T^{-1}\Sigma pe^{-\epsilon/kT}$ due to the levels F_1, F_2 and F_3 respectively corresponding to the vibrational quantum number $v = 0$ and $v = 1$. The contri-

[1] *J. Am. Chem. Soc.*, **50**, 101 (1928).

[2] Mulliken, *Phys. Rev.*, **32**, 880 (1928).

[3] *Proc. Nat. Acad. Sci.*, **13**, 670 (1927).

[4] *J. Am. Chem. Soc.*, **51**, 2300 (1929).

<div align="center">

TABLE VIII *

Sᴜᴍs ɪɴ ᴛʜᴇ Eɴᴛʀᴏᴘʏ Eǫᴜᴀᴛɪᴏɴ ꜰᴏʀ Oxʏɢᴇɴ ᴀᴛ 298.16° K

</div>

	$\Sigma p e^{-\epsilon/kT}$	$\dfrac{1}{kT} \Sigma \epsilon p e^{-\epsilon/kT}$
F_1, $v = 0$	83.831	77.959
F_2, $v = 0$	72.882	72.628
F_3, $v = 0$	63.155	67.363
	219.868	217.950
$(F_1 + F_2 + F_3)$, $v = 1$	0.125	1.055
$(F_1 + F_2 + F_3)$, $v = 2$	.000	.000
	219.993	219.006

butions for $v > 1$ are negligible. The sums are obtained by adding the parts due to F_1, F_2 and F_3 and are then substituted in (31.7).

The entropy of oxygen at 298.16° K obtained in this way is 49.03 cal. per degree per mole. The reader will find it of value to check this result as well as the entries of Table VIII.

(46) **The Entropy of Hydrogen and the Third Law of Thermodynamics**: As has already been seen, when the nuclear spin varieties of hydrogen ($i = \frac{1}{2}$, $n = 2$) are brought to equilibrium at high temperatures, one quarter of the hydrogen consists of molecules with the single antisymmetric nuclear spin wave function (para) and three quarters consists of molecules with equal parts of the three symmetric nuclear spin wave functions (ortho). There are thus $2^2 = 4$ nuclear spin wave functions among which the molecules are equally divided. Since ordinary hydrogen is formed under these conditions this situation exists in ordinary hydrogen. In the absence of a magnetic field the nuclear spin functions cannot change, one into the other, as the temperature is lowered into regions where the distribution can no longer be regarded as classical: hence, the nuclear spin states are still in equal ratios and no longer in equilibrium as the gas is cooled. The molecules of ordinary gaseous hydrogen must be considered as equally divided between four kinds, and the entropy of each must be calculated separately. Let the molal entropies of the gases be S_1, S_2, S_3 and S_4; the total entropy of a mole of mixture will then be [1]

$$S = \frac{1}{4}(S_1 + S_2 + S_3 + S_4) + R \ln 4. \qquad (46.1)$$

Let S_1 be the molal entropy of the molecules with the antisymmetric nuclear wave function. The translational entropy is given by equation (44.3) with $p_s = 1$, and the rotational and vibrational entropy by equation (31.7) in which the sums are taken only over even rotational states. The entropies S_2, S_3 and S_4 are respectively the molal entropies of the molecules with the three

---

* The values given in this table are given in terms of earlier values of the fundamental constants. (See Giauque and Johnston, *J. Am. Chem. Soc.*, **51**, 2300 (1929)).

[1] Giauque, *J. Am. Chem. Soc.*, **52**, 4816 (1930).

kinds of symmetric wave functions. The translational entropy of each is again given by equation (44.3) with p_s equal to unity, but the rotational and vibrational entropies are now given by equation (31.7) with the sums carried out over the odd rotational levels. The entropy of hydrogen in the ideal gas state is, therefore, given by

$$S = S_t + \tfrac{1}{4}R \left[\frac{\Sigma p \epsilon e^{-\epsilon/kT}}{\Sigma p e^{-\epsilon/kT}} - \ln \Sigma p e^{-\epsilon/kT} \right]_{\text{even}}$$
$$+ \tfrac{3}{4}R \left[\frac{\Sigma p \epsilon e^{-\epsilon/kT}}{\Sigma p e^{-\epsilon/kT}} - \ln \Sigma p e^{-\epsilon/kT} \right]_{\text{odd}} + R \ln 4, \quad (46.2)$$

where the second and third terms of the right-hand side are respectively the rotational entropies due to the para and ortho rotational states, and the last term is the entropy of mixing. Only at temperatures where the distribution may be regarded as classical do the two bracketed quantities in equation (46.2) become equal: such temperatures are reached at about 300° K.

In this way the entropy of hydrogen at 298.16° K in the ideal gas state at 1 atm. is found to be 33.98 cal./deg./mole, the entropy due to nuclear spin being included.

If the situation in the crystal of ordinary hydrogen is that pictured for the general case, the value for the entropy of hydrogen just obtained should exceed the third law value by $R \ln 4 = 2.75$ cal./deg./mole, which would be the entropy of the crystal at very low temperatures due to nuclear spin. However it appears that ortho-hydrogen rotates in the crystal at low temperatures (10° K), and is in the rotational level with $J = 1$. Thus there are $2J + 1 = 3$ rotational states of ortho-hydrogen of approximately the same energy but differing in their orientation in space. Each of the three varieties of ortho-hydrogen distinguished by their nuclear spin wave functions may have any one of these three rotational levels, so that nine kinds of molecules are possible all with the same probability. In other words nine wave functions correspond to ortho-hydrogen. These constitute three quarters, i.e., nine twelfths, of the total, so that each kind forms one twelfth of the total. The para-hydrogen is in the lowest rotational state and, therefore, has only one rotational wave function, viz., that corresponding to no rotation at all. Because there is only one nuclear spin wave function, the antisymmetric, only one wave function corresponds to the para-hydrogen which forms one quarter, i.e., three twelfths, of the total. The entropy of mixing of the different kinds of hydrogen is then

$$S = - R[\tfrac{3}{12} \ln \tfrac{3}{12} + 9(\tfrac{1}{12} \ln \tfrac{1}{12})]$$
$$= - R[\tfrac{1}{4} \ln \tfrac{1}{4} + \tfrac{3}{4} \ln \tfrac{1}{12}] = 4.39 \text{ cal./deg./mole.} \quad (46.3)$$

Since any one of the kinds of hydrogen would be assigned zero entropy at the absolute zero, this is the entropy of the crystal instead of the $R \ln 4$ (2.76 cal./deg./mole) which would be present if the ortho-hydrogen was limited to one kind of rotational level. Thus the entropy measured using the *third law* and

the calorimetric data from 12° K to 298.16° K should be 33.98 − 4.39 = 29.59 cal./deg./mole at 298.16° K.   The value actually found is 29.74 cal./deg./mole.

At 10° K the crystal of hydrogen with its nine kinds of ortho-hydrogen behaves as though the three rotational energy levels had the same energy. They are present in equal amounts and the heat capacity shows nothing to indicate that there will eventually be a reorientation to a single rotational level with $J = 1$ due to a slight energy difference between the three rotational levels. Thus extrapolation is made on this basis so that the whole third law calculation is based correctly on the situation given.   From measurements on solid hydrogen (25 per cent ortho, 75 per cent para) in the region 2° K to 10° K, it has been found [1] that at 2° K the heat capacity of hydrogen is many times that predicted on the basis of the theory of the heat capacity of crystalline solids, and that the effect persists up to almost 10° K.   The results are shown in Fig. 8 (curve *b*).   This discrepancy is undoubtedly due to the fact that the
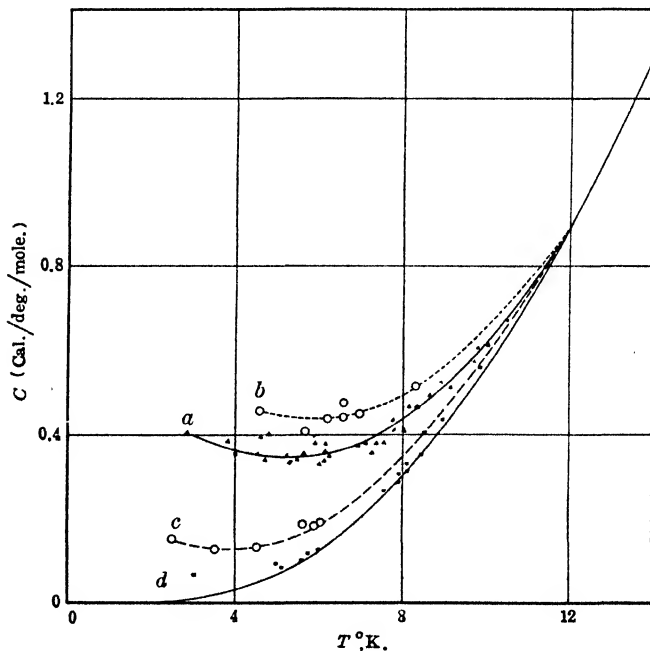
Fig. 8.   Heat Capacity of Solid Hydrogen: Curve *b*—Ordinary Hydrogen; Curve *a*—50% Para-hydrogen; Curve *c*—80% Para-hydrogen; Curve *d*—100% Para-hydrogen

three rotational levels of ortho-hydrogen with $J = 1$ do not have exactly the same energy in the crystal.   In the region below 10° K this energy difference between the three quantum states belonging to the rotational level $J = 1$ causes

[1] Mendelssohn, Ruehmann and Simon, *Z. physik. Chem.*, **B, 15,** 121 (1931).

the Boltzmann law to favor the lowest of these levels because now the temperature is very low and we are dealing with a ratio of numbers in the states given by $e^{-\Delta E/kT}$. In other words the three rotational levels are tending to line up and at 2° K this process is occurring to a marked degree. The additional heat capacity, over that predicted by the Debye theory of crystalline solids (cf. p. 620), is due to the energy required to raise the lowest of the three rotational levels into the other two of higher energy with increasing temperature, as the Boltzmann distribution law requires.

It has already been pointed out, that, if hydrogen is cooled down to 10° K in the presence of a catalyst which allows the molecules to change their spin wave function, practically all the molecules end up in the lowest ($J = 0$) rotational level which has the antisymmetric wave function for the nuclear spins. If the catalyst is removed while the temperature is low, and the gas is allowed to warm up, the antisymmetric wave functions cannot change into symmetric ones and the gas has only even rotational levels; in other words it is para-hydrogen. Mendelssohn, Ruhemann and Simon measured the heat capacity of pure solid para-hydrogen between 2° K and 10° K and found a heat capacity curve in agreement with the Debye theory. This is to be expected as the solid contains only molecules which can assume the rotational energy level with $J = 0$ which has no degeneracy ($2J + 1 = 1$). At these temperatures, therefore, practically all the molecules are in the lowest rotational level since the level with $J = 2$ has a much higher energy; hence, only the elastic vibrations of the solid determine the specific heat. The results for pure para-hydrogen are shown on curve d of Fig. 8 in which (a) and (c) are for 50 per cent and 20 per cent ortho-hydrogen respectively. The deviation from the curve for para-hydrogen, as would be expected, is proportional to the percentage of ortho-hydrogen.

If curve (b) which is for ordinary hydrogen could be extended to the absolute zero the entropy increase from 0° K to 12° K could be obtained from it and used in place of the value obtained by extrapolation of the results which only extended to 12° K to obtain the entropy of hydrogen at 298.16° K. At 12° K the rotational levels with $J = 1$ have not yet started to line up so that extrapolation was made to a solid at the absolute zero with these three levels of different orientations of ortho-hydrogen present in equal amounts. This solid has an entropy given by equation (46.3). On the other hand the solid obtained by *experimental* cooling to 0° K has 25 per cent of para-hydrogen in the level $J = 0$ and 75 per cent of ortho-hydrogen in only *one* of the levels with $J = 1$ namely that of lowest energy but equally distributed among the symmetrical nuclear spin wave functions. Thus there are four kinds of hydrogen present in equal amounts and the entropy of the solid is

$$S = - R(\tfrac{1}{4} \ln \tfrac{1}{4}). \tag{46.4}$$

This is just exactly the entropy due to nuclear spin; hence, the entropy of ordinary gaseous hydrogen obtained using experimental heat capacity data

down to well below 2° K would be the entropy of gaseous hydrogen less that due to nuclear spin namely $33.98 - R \ln 4 = 31.23$ cal./deg./mole.

(47) Entropy of Molecules Having Classical Excited Rigid Rotation—Sulfur Dioxide: The application of equation (32.18) to the rotational entropy of a classically excited diatomic molecule and to rigid polyatomic molecules is easily made by substitution of the respective partition functions as given by equations (41.1) and (41.2). In this manner the following equations are obtained for rotational entropy.

Diatomic Molecules:

$$S_r = R + R \ln \left[\frac{8\pi^2 I k T}{\sigma h^2} \right] \tag{47.1}$$

or, inserting the numerical values of the constants,

$$S_r = R[\ln IT - \ln \sigma + 89.408]. \tag{47.2}$$

Rigid Polyatomic Molecules:

$$S_r = {}^3{}_2 R + R \ln \frac{8\pi^2}{\sigma h^3} (8\pi^3 ABC)^{1/2} (kT)^{3/2} \tag{47.3}$$

or, with the numerical values of the constants substituted,

$$S_r = R[{}^3\!\!\!/_2 \ln T + \tfrac{1}{2} R \ln ABC - \ln \sigma + 134.687]. \tag{47.4}$$

These values must be combined with the translational entropy as given by equation (44.3) and the vibrational entropy in order to obtain the total entropy.

The vibrational entropy for a single mode of vibration is simply computed by substituting the vibrational partition function into equation (32.18); thus

$$S_v = R \left[\ln q_v + T \frac{\partial \ln q_v}{\partial T} \right] = \frac{Rx}{e^x - 1} - R \ln (1 - e^{-x}). \tag{47.5}$$

Values of the quantities involved in this equation are tabulated in Appendix I.

As an example of the method of computation we shall consider the entropy of sulfur dioxide at 298.15° K; this is a nonlinear polyatomic molecule and equation (47.4) applies. Combining equation (47.4) with equation (44.3), taking p_s equal to unity and R as 1.9869, we obtain for the total entropy

$$S = \tfrac{3}{2} \times 4.575 \log M + 4 \times 4.575 \log T - 4.575 \log P$$
$$+ \tfrac{1}{2} \times 4.575 \log ABC - 4.575 \log \sigma + 265.289 + \sum_\nu S_\nu,$$

where S_ν is the entropy of the mode of vibration of fundamental frequency ν and the summation is extended over three such modes in this case.

The distance between the sulfur and oxygen atoms in sulfur dioxide is 1.46 ± 0.02 Å and the bond angle is $122 \pm 5°$;[1] using these data ABC is

[1] Cross and Brockway, *J. Chem. Phys.*, **3**, 821 (1935).

found to be 9.819×10^{-116} g.cm.^{2}; the symmetry number σ is 2, and the molecular weight is 64.06 g.

Sulfur dioxide has three atoms and therefore 3×3, i.e., 9, degrees of freedom. Six of these are for translation and rotation so that the remaining three are vibration: the fundamental vibration frequencies are $\nu_1 = 525$, $\nu_2 = 1152$ and $\nu_3 = 1361$ cm.$^{-1}$.

Table IX summarizes the calculation of the entropy at 298.15° K based on these molecular data.[1]

TABLE IX

THE ENTROPY OF SULFUR DIOXIDE FROM SPECTROSCOPIC AND MOLECULAR DATA
AT 298.15° K AND 1 ATM.

	Entropy Cal./Deg./Mole
$\frac{3}{2} \times 4.575 \log M$	12.40
$4 \times 4.575 \log 298.15$	45.28
$-4.575 \log P$	0.00
$\frac{1}{2} \times 4.575 \log ABC$	-263.08
$-4.575 \log 2$	-1.38
265.289	265.289
	58.51
S_ν for 525 cm.$^{-1}$	0.600
S_ν for 1152 cm.$^{-1}$	0.051
S_ν for 1361 cm.$^{-1}$	0.022
Total	59.18

(48) Entropy Due to Electron Degeneracy: At high temperatures equation (47.2) with $\sigma = 2$ can be used to calculate the entropy of oxygen; to this must be added the translational contribution, as calculated from equation (44.3), and the vibrational contribution. In this calculation we assume that the three states of oxygen, differing in the orientation of the two unpaired electron spins, have the same energy. Thus p_s must be placed equal to three in equation (44.3).

THE THIRD LAW AND STATISTICAL MECHANICS

(49) The Comparison of Third Law Entropies with Those from Statistical Mechanics: According to the discussion of the previous paragraphs the third law of thermodynamics is a direct result of statistical mechanics and the second law of thermodynamics if it states that the entropies of "perfect" crystals at the absolute zero are zero. By a "perfect" crystal is meant one that has an ordered arrangement. That the law thus stated is true is demonstrated by the number of cases in which entropies of gases as obtained from the calorimetric data down to low temperatures ("calorimetric" entropies) agree with those obtained from the spectroscopic and molecular data ("spectroscopic" entropies).

Table X compares the "spectroscopic" entropies of a number of gases, with

[1] Giauque and Stephenson, *J. Am. Chem. Soc.*, **60**, 1389 (1938).

TABLE X

ENTROPIES FROM SPECTROSCOPIC DATA COMPARED WITH THOSE FROM THE THIRD LAW
OF THERMODYNAMICS AT 298.15° K AND 1 ATM.

Ideal Gas	Practical Entropy (Ideal Gas at 1 Atm.) Cal./Deg./Mole		Discrepancy Spect. − Cal. Cal./Deg./Mole	Notes on the Discrepancy
	Spectroscopic	Calorimetric		
[a]HCl	44.64	44.5		
[b]HBr	47.48	47.6		
[c]HI	49.4	49.5		
[d]N_2	45.78	45.9		
[e]O_2	49.03	49.1		
[f]Cl_2	53.31	53.32		
[g]H_2	31.23	29.74	1.49	$-R(\frac{1}{4}\ln\frac{1}{4}+\frac{3}{4}\ln\frac{1}{12}-\ln\frac{1}{4})=1.63$
[h]CO	47.31	46.2	1.11	$R\ln 2 = 1.38$
[i]H_2O	45.10	44.28	0.82	$R\ln\frac{6}{4}=0.806$
[j]H_2S	49.10	49.15		
[k]CO_2	51.07	51.11		
[l]COS	55.37	55.27		
[m]N_2O	52.58	51.44	1.14	$R\ln 2 = 1.38$
[n]HCN	48.23	47.92		
[o]NH_3	45.94	45.91		
[p]PH_3	50.5	50.35		
[q]$(CN)_2$	57.88	57.64		
[r]CH_4	44.35	44.30		
[s]SO_2	59.18	59.24		
[t]C_2H_4	52.47	52.48		
[u]CH_3Br	58.74	58.61		
[v]CH_3Cl	55.98	55.94		

[a] Giauque and Overstreet, *J. Am. Chem. Soc.*, **54**, 1731 (1932); Giauque and Wiebe, *ibid.*, **50**, 101 (1928).

[b] Giauque and Wiebe, *ibid.*, **50**, 2193 (1928).

[c] Giauque and Wiebe, *ibid.*, **51**, 1441 (1929).

[d] Giauque and Clayton, *ibid.*, **55**, 4875 (1933).

[e] Giauque and Johnston, *ibid.*, **51**, 2300 (1929).

[f] Giauque and Overstreet, *ibid.*, **54**, 1731 (1932); Giauque and Powell, *ibid.*, **61**, 1970 (1939).

[g] Giauque, *ibid.*, **52**, 4816 (1930).

[h] Clayton and Giauque, *ibid.*, **54**, 2610 (1932); Clayton and Giauque, *ibid.*, **55**, 5071 (1933).

[i] Giauque and Ashley, *Phys. Rev.*, **43**, 81 (1933); Giauque and Stout, *J. Am. Chem. Soc.*, **58**, 1144 (1936); Giauque and Archibald, *ibid.*, **59**, 561 (1937); Giauque, *ibid.*, **59**, 1157 (1937).

[j] Clusius and Frank, *Naturwiss.*, **24**, 62 (1936); Giauque and Blue, *J. Am. Chem. Soc.*, **58**, 831 (1936).

[k] Giauque and Egan, *J. Chem. Phys.* **5**, 45 (1937).

[l] Kemp and Giauque, *J. Am. Chem. Soc.*, **59**, 79 (1937).

[m] Blue and Giauque, *ibid.*, **57**, 991 (1935).

[n] Giauque and Ruehrwein, *ibid.*, **61**, 2626 (1939).

[o] Giauque, Blue and Overstreet, *Phys. Rev.*, **38**, 196 (1931); Overstreet and Giauque, *J. Am. Chem. Soc.*, **59**, 254 (1937).

[p] Stephenson and Giauque, *J. Chem. Phys.*, **5**, 149 (1937).

the "calorimetric" entropies. In all cases the "calorimetric" values were obtained from data down to at least 14° K and have been corrected to the ideal gas state at one atm. The "spectroscopic" entropies are the "practical" entropies at 1 atm. obtained by subtracting the limiting high temperature value of the entropy due to nuclear spin from the total entropy. Except for hydrogen, this is the value obtained by neglecting the effect of the nuclear wave functions altogether. Column four of Table X gives the discrepancy between the "spectroscopic" and "calorimetric" entropies. We have already seen the cause for the discrepancy in the case of hydrogen, namely, that more entropy exists in the solid state considered (extrapolated) than the nuclear spin entropy of $R \ln 4$. This excess is due to the rotation of the ortho-hydrogen. The clean-cut explanation of this discrepancy is a strong indication of the correctness of the third law. The discrepancies in the case of carbon monoxide, nitrous oxide and water can now be considered.

(50) **The Entropy of Imperfect Crystals at the Absolute Zero**: Suppose that a crystal does not have its molecules in a completely ordered array due to the fact that the molecules are differently oriented. Let us suppose that there are p possible orientations of equal energy. We can consider the crystal as a solid solution, perfect in nature, of p possible molecular species differentiated by their orientation. The additional entropy in the solid is then the entropy of mixing of these species. If there is a mole fraction x_i of the ith kind of molecule, this entropy of mixing is

$$S_m = - R \sum_{i=1}^{i=p} x_i \ln x_i. \tag{50.1}$$

In carbon monoxide the oxygen atom is surrounded by the same number of electrons as the carbon atom so that a rotation of the molecule through 180° in the crystal will produce little change in energy. Thus, by the Boltzmann distribution law there will be no discrimination between the oxygen and carbon ends of the molecule in the crystal until the temperature is sufficiently low to make appreciable the small energy difference produced by rotation of the molecule through 180°. If the energy difference were truly zero, there would be two types of carbon monoxide molecule at the absolute zero, differing in their orientation by 180°, randomly distributed throughout the crystal. The residual entropy would thus be $R \ln 2$ by equation (50.1). On the other hand, at very low temperatures it becomes increasingly difficult for the molecule to turn in the crystal as the temperature is lowered. Thus, at temperatures where the small energy difference between the two orientations tends to cause

---

[q] Ruehrwein and Giauque, *J. Am. Chem. Soc.*, **61**, 2940 (1939).

[r] Giauque, Blue and Overstreet, *Phys. Rev.*, **38**, 196 (1931).

[s] Cross, *J. Chem. Phys.*, **3**, 825 (1935); Giauque and Stephenson, *J. Am. Chem. Soc.*, **60**, 1389 (1938).

[t] Egan and Kemp, *ibid.*, **59**, 1264 (1937).

[u] Egan and Kemp, *ibid.*, **60**, 2097 (1938).

[v] Messerly and Aston, *ibid.*, **62**, 886 (1940).

all the molecules to be arranged in a regular manner throughout the crystal, it is likely that the rate of turning of the molecules would be inappreciable. In this situation the crystal would be cooled to the absolute zero in a non-equilibrium configuration which had a residual entropy of $R \ln 2$. In this manner the discrepancy between the calorimetric and spectroscopic entropies can be explained.

The discrepancy with nitrous oxide, which is a linear molecule, NNO, is similarly explained. Figure 9 is a schematic diagram of the situation at low temperatures in the case of crystalline nitrous oxide. No matter how large the unit chosen is taken, it is not repeated in the crystal.

```
NNO,  NNO,  ONN,  NNO,  ONN,  ONN,  ONN,  NNO
NNO,  ONN,  ONN,  ONN,  NNO,  ONN,  NNO,  NNO
ONN,  ONN,  ONN,  NNO,  ONN,  ONN,  ONN,  ONN
NNO,  NNO,  NNO,  NNO,  ONN,  ONN,  NNO,  ONN
ONN,  NNO,  NNO,  NNO,  NNO,  NNO,  ONN,  NNO
etc.,  etc.
```
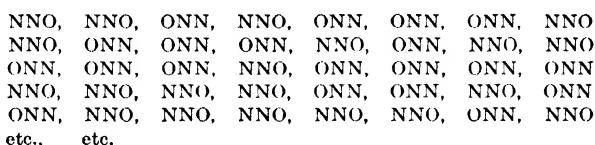
FIG. 9. SCHEMATIC ARRANGEMENT IN ONE PLANE OF MOLECULES IN CRYSTALLINE NITROUS OXIDE AT LOW TEMPERATURES

The discrepancy in the case of water can be explained in a similar manner but here the arrangements to be considered are more complicated. Theory predicts a false equilibrium with a random orientation corresponding to an entropy at the absolute zero of $R \ln \frac{3}{2} = 0.806$ cal./deg./mole.[1]

If there are several states (say ω_0' in number) of equal energy due to electron spin, corresponding to the lowest electronic level, these states may be mixed in equal quantities in the crystal down to the lowest temperatures used in third law work (usually 10° to 12° K). Thus extrapolation is made on this basis in obtaining the third law entropy, and the crystal form to which the extrapolation applies has an entropy of $R \ln \omega_0'$. Crystalline oxygen *does not* belong to this class as the degeneracy of the lowest electronic state *in the gas* ($^3\Sigma$) is removed in the crystal. However, certain salts of rare earths undoubtedly belong to this class. In these cases the entropy $R \ln \omega_0'$ can be removed by going to sufficiently low temperatures. For example, ω_0' for gadolinium sulfate is eight but part of this degeneracy can · be removed by cooling to about 0.1° K. Extrapolation of third law data down to 0.1° K gives an entropy only $R \ln 2$ too small but extrapolation of data down to 10° K gives an entropy for a gadolinium salt which is $R \ln 8$ too small. This subject is taken up in detail in a later paragraph.

(51) **The Classical Rotational Partition Function for Molecules With Free Internal Rotation:** We shall assume that all the rotational degrees of freedom are separable from the vibrational but not necessarily from each other; thus,

$$Q = Q_r(q_v)_r(q_v)_2 \cdots (q_v)_k, \qquad (51.1)$$

[1] Pauling, *J. Am. Chem. Soc.*, **57**, 2680 (1935).

where Q_r is the partition function for all rotational degrees of freedom. We shall now evaluate Q_r for the classical case on the assumption that no potentials hinder the internal rotations.

Let θ, ϕ and ψ (the Eulerian angles) which orient the molecule as a whole be denoted by q_1, q_2 and q_3 and let the angles ω_1, ω_2, $\cdots$, ω_{s-3} which orient the internally rotating groups be denoted by q_4, q_5, $\cdots$, q_s. The classical rotational kinetic energy is given by

$$T = \tfrac{1}{2} \sum_{i,j=1}^{s} R_{ij}\dot{q}_i\dot{q}_j, \tag{51.2}$$

where the R_{ij} contain the q's. Let the momenta corresponding to q_1, $\cdots$, q_s be given by p_1, $\cdots$, p_s; there are then s equations of the form

$$p_i = \frac{\partial T(q_i\dot{q}_i)}{\partial \dot{q}_i}. \tag{51.3}$$

The rotational kinetic energy is given in terms of the momenta by

$$T = \tfrac{1}{2} \sum_{i,j=1}^{s} P_{ij}p_ip_j, \tag{51.4}$$

where the P_{ij} contain the q's and may be obtained by solving equations (51.3) (after differentiating) for the $\dot{q}$'s in terms of the p's and substituting in equation (51.2). The P_{ij}'s are thus expressed in terms of the determinant

$$[R] = \begin{vmatrix} R_{11} & R_{12} & \cdots & R_{1s} \\ R_{21} & R_{22} & \cdots & R_{2s} \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ R_{s1} & R_{s2} & \cdots & R_{ss} \end{vmatrix} \tag{51.5}$$

and its first minors.

If the internal rotation is free there is no potential energy and the classical value of Q_r is then given by

$$Q_r = \frac{1}{\sigma h^s} \int \cdots \int e^{-\Sigma P_{ij}p_ip_j/2kT} \, dq_1 \cdots dq_s dp_1 \cdots dp_s.$$

It has been shown by Eidinoff and Aston [1] that the integration with respect to all of the momenta can be carried out for the general case giving

$$Q_r = \frac{1}{\sigma} \left(\frac{2\pi kT}{h^2} \right)^{s/2} \int \cdots \int [R]^{1/2} dq_1 \cdots dq_s, \tag{51.6}$$

---

[1] *J. Chem. Phys.*, **3**, 379 (1935).

where σ is the number of equivalent positions of the molecule that can be produced by turning about axes of symmetry counting the σ' that can be produced by turning the whole molecule and the σ'' that can be produced by internal rotation, i.e., $\sigma = \sigma'\sigma''$, or

$$Q_r = \frac{1}{\sigma}\left(\frac{2\pi kT}{h^2}\right)^{s/2} \int \cdots \int [R]^{1/2} d\theta d\phi d\psi d\omega_1 \cdots d\omega_{s-3}. \qquad (51.7)$$

Kassel [1] has shown that the integration with respect to θ, ϕ and ψ may be performed, giving

$$Q_r = \frac{1}{\sigma}\left(\frac{2\pi kT}{h^2}\right)^{s/2} 8\pi^2 \int_0^{2\pi} \cdots \int_0^{2\pi} [S]^{1/2} d\omega_1 \cdots d\omega_{s-3}, \qquad (51.8)$$

where $[S]$ is defined by

$$[S] = \begin{vmatrix} K_{11} & \cdots & K_{1,s-3} & D_1 & E_1 & F_1 \\ \cdot & & \cdot & \cdot & \cdot & \cdot \\ \cdot & & \cdot & \cdot & \cdot & \cdot \\ \cdot & & \cdot & \cdot & \cdot & \cdot \\ K_{s-3,1} & \cdots & K_{s-3,s-3} & D_{s-3} & E_{s-3} & F_{s-3} \\ D_1 & \cdots & D_{s-3} & A' & -\{xy\} & -\{xz\} \\ E_1 & \cdots & E_{s-3} & -\{xy\} & B' & -\{yz\} \\ F_1 & \cdots & F_{s-3} & -\{xz\} & -\{yz\} & C' \end{vmatrix}$$

where K_{ij} is the coefficient of the term $\dot{\omega}_i\dot{\omega}_j$ in the kinetic energy expression and D_i, E_i and F_i are such that the total contributions of the internal rotations to the angular momenta about axes X, Y and Z fixed in the molecule are respectively

$$\sum_{i=1}^{i=s-3} D_i\dot{\omega}_i, \qquad \sum_{i=1}^{i=s-3} E_i\dot{\omega}_i, \qquad \text{and} \qquad \sum_{i=1}^{i=s-3} F_i\dot{\omega}_i.$$

The terms A', B' and C' are the moments of inertia of the whole molecule about these axes (external moments) while the terms $\{xy\}$ etc., are the corresponding products of inertia, i.e.,

$$A' = \sum_k m_k(y_k^2 + z_k^2)$$

and

$$\{xy\} = \sum_k m_k x_k y_k,$$

[1] *Ibid.*, **4**, 276 (1936).

where x_k, y_k and z_k are the coordinates of the kth atom. The terms D_i, E_i and F_i consequently arise from the interaction of the external rotations with the internal rotations.

If the rotations within the molecule are only those of rigid groups which are attached to a single atom or a rigid framework of atoms, $[S]$ may be further simplified: examples are tetramethyl methane, trimethyl ethylene, isopropyl alcohol (but *not* butane which consists of a methyl and an ethyl group which itself has an internal rotation, substituted in methane). Under these circumstances $[S]$ is given by

$$[S] = K_1 K_2 \cdots K_{s-3} \begin{vmatrix} A' - \{\lambda\lambda\} & -\{xy\} - \{\lambda\mu\} & -\{xz\} - \{\lambda\nu\} \\ -\{xy\} - \{\lambda\mu\} & B' - \{\mu\mu\} & -\{yz\} - \{\mu\nu\} \\ -\{xz\} - \{\lambda\nu\} & -\{yz\} - \{\mu\nu\} & C' - \{\nu\nu\} \end{vmatrix}, \quad (51.9)$$

where K_1, K_2, K_3, etc. are the moments of the $(s - 3)$ rotating groups about the bonds joining them to the rigid framework of atoms and

$$\{\lambda\mu\} = \sum_{i=1}^{i=s-3} \lambda_i \mu_i K_i,$$

$$\{\lambda\lambda\} = \sum_{i=1}^{i=s-3} \lambda_i \lambda_i K_i,$$

$$(51.10)$$

in which λ_i, μ_i and ν_i are the direction cosines of the axis of the ith top with respect to the axes X, Y and Z fixed in the molecule. Writing $[\Omega]$ for the determinant on the right-hand side of equation (51.9), this becomes

$$[S] = K_1 K_2 \cdots K_{s-3} [\Omega]. \quad (51.10)$$

The determinant $[\Omega]$ depends upon $\omega_1, \omega_2, \cdots, \omega_s$ because A', B', C', $\{xy\}$, $\{yz\}$ and $\{xz\}$ depend on the phase of revolution of the rotating groups.

If the rotating group is one, such as a methyl group, for which the axis of rotation is a principal axis, the value of Ω is independent of the phase of the rotation as given by the angle ω_1. Integration with respect to this variable merely produces multiplication of the integrand by 2π. If, therefore, all the rotating groups are of such a kind, equation (51.8) becomes

$$Q_r = \frac{1}{\sigma} \left(\frac{2\pi kT}{h^2} \right)^{s/2} 8\pi^2 (2\pi)^{s-3} \{ K_1 K_2 \cdots K_{s-3} [\Omega] \}^{1/2}. \quad (51.11)$$

It will be noted that equation (51.11) differs from equation (41.2) by the factor $(2\pi)^{(s-3)}$ times $(2\pi kT/h^2)^{(s-3)/2}$ times the square root of the product of the moments of the internally rotating groups about their axis of rotation, and also that $[\Omega]$ replaces, but is only slightly different from, ABC as given by

equation (41.3).   The determinant $[\Omega]$ contains the terms λ_i, μ_i etc., while ABC as given by equation (41.3) does not.   These terms are due to the interaction between the external and internal rotations.

If the terms in λ_i, μ_i, etc. may be neglected from $[\Omega]$, Q_r takes on the form

$$Q_r = \left[\frac{8\pi^2}{\sigma'} \left(\frac{2\pi kT}{h^2} \right)^{3/2} (ABC)^{1/2} \right] \times \prod_{i=1}^{i=s-3} \left[\frac{2\pi}{\sigma''} \left(\frac{2\pi kT}{h^2} \right)^{1/2} K_i^{1/2} \right], \quad (51.12)$$

in which A, B, C are the principal external moments; hence,

$$Q_r = (Q_{r \text{ ext.}}) \prod_{i=1}^{i=s-3} r_i, \quad (51.13)$$

where $Q_{r \text{ ext.}}$ is given by (41.2) with σ' replacing σ, and

$$r_i = \frac{2\pi}{\sigma''} \left(\frac{2\pi kT}{h^2} \right)^{1/2} K_i^{1/2} \quad (51.14)$$

is the partition function for the internal rotation of a group whose moment is K_i about its axis of rotation.   This approximation is possible when the external moments are large, as they are in tetramethyl methane, and the moments of the internally rotating groups are small.   A better approximation is obtained by using the reduced moments of the rotation about the respective axis instead of K_i.   These are defined by

$$I_{\text{red.}} = \frac{KI_B}{K + I_B}, \quad (51.15)$$

where I_B is the moment, about the axis of rotation, of all the molecules except the group where internal rotation is being considered.   In using equation (51.14) $I_{\text{red.}}$ is always employed instead of K_i.   Even if the internally rotating groups are not symmetrical, as is the case with the hydroxyl group, equation (51.12) is valid if the groups have comparatively small moments.   Evidently, then, for a rigid rotor, (51.6) reduces to (41.2) and the above treatment is a proof of the latter equation.

By substituting equation (51.6) into equation (34.7) it is seen that

$$E_r = \frac{s}{2} RT, \quad (51.16)$$

while substitution into (34.8) gives

$$C_r = \frac{s}{2} R. \quad (51.17)$$

Both of these results follow directly from the principle of equipartition.

(52) **The Entropy of Complex Molecules with Classically Excited Free Internal Rotation—Silicon Tetramethyl:** The procedure differs from that used

in the case of a rigid rotor as exemplified by sulfur dioxide in that, in general, equation (51.6) replaces (41.2) for the rotational partition function. For symmetrical internally rotating groups attached to a rigid frame (51.11) is used instead. In the latter case, the expression for the rotational entropy to be used in place of (47.3) is

$$S_r = \frac{s}{2}R + R \ln\left(\frac{2\pi kT}{h^2}\right)^{s/2} 8\pi^2 (2\pi)^{(s-3)} \{K_1 K_2 \cdots K_{s-3}[\Omega]\}^{1/2} - R \ln \sigma, \quad (52.1)$$

which, separating the constants, becomes

$$S_r = \frac{s}{2}R \ln T + \frac{R}{2} \ln K_1 K_2 \cdots K_{s-3}[\Omega]$$
$$- R \ln \sigma - (s - 3)45.292R + 134.687R. \quad (52.2)$$

As an example we shall outline the method of calculation of the entropy of silicon tetramethyl; this substance has three external and four internal rotations making a total of seven. The Z axis is taken along the bond between the silicon atom and carbon atom number one, with the origin at the silicon atom. The X axis is chosen so that the XZ plane is coincident with that determined by the silicon atom and carbon atoms one and four. Carbon atom number two is placed so that its y-coordinate is negative. Silicon tetramethyl has been shown to have tetrahedral angles between the carbon-silicon bonds and thus is a symmetrical top. Therefore, any X, Y and Z axes are principal axes and $\{xy\} = \{yz\} = \{zx\} = 0$. The moments $A = B = C$ are found to be 283.1×10^{-40} g.cm.^{2} from the bond distances (C $-$ Si, 1.93; C $-$ H, 1.09 Å).

It is easily shown that ν_1 (the direction cosine of the bond between the silicon atom and carbon atom number one with the Z axis) is unity while $\nu_2 = \nu_3 = \nu_4 = \frac{1}{3}$. Further,

$$\lambda_1 = 0, \qquad \lambda_2 = \lambda_3 = (\tfrac{2}{9})^{1/2}, \qquad \lambda_4 = 2(\tfrac{2}{9})^{1/2}$$

and

$$\mu_1 = 0, \qquad \mu_2 = -(\tfrac{2}{3})^{1/2}, \qquad \mu_3 = (\tfrac{2}{3})^{1/2}, \qquad \mu_4 = 0.$$

Thus,

$$\begin{aligned}\{\lambda\nu\} &= (\lambda_1\nu_1 + \lambda_2\nu_2 + \lambda_3\nu_3 + \lambda_4\nu_4)\\ &= 0 \times 1 + (\tfrac{2}{9})^{1/2}\,\tfrac{1}{3} + (\tfrac{2}{9})^{1/2}\,\tfrac{1}{3} - 2(\tfrac{2}{9})^{1/2}\,\tfrac{1}{3}\\ &= 0.\end{aligned}$$

Similarly

$$\{\lambda\mu\} = 0 \qquad \text{and} \qquad \{\mu\nu\} = 0,$$

while

$$\{\lambda\lambda\} = \{\mu\mu\} = \{\nu\nu\} = \tfrac{4}{3}K.$$

The value of K is readily calculated to be 5.27×10^{-40} if the C $-$ H distance is taken as 1.09 Å and tetrahedral angles are assumed between C $-$ H bonds;

thus

$$[S] = (5.27 \times 10^{-40})^4 \begin{vmatrix} M & 0 & 0 \\ 0 & M & 0 \\ 0 & 0 & M \end{vmatrix}$$

[where $\quad M = (283.1 - \tfrac{1}{3} \times 5.27) \times 10^{-40}$]

or

$$[S] = (5.27 \times 10^{-40})^4 (210.5 \times 10^{-115}) = 162.37 \times 10^{-272}.$$

The symmetry number is $\sigma = \sigma'\sigma'' = 12 \times 3^4$. The factor $\sigma'' = 3^4$ arises because for each of the twelve sets of exchanges of identical atoms produced by rotation of the molecule as a whole, there are three positions produced by rotation of each methyl group (3^4 in all) which merely differ by interchanges of atoms.

The vibrational entropy is obtained as described before. The fundamental frequencies of vibration of the carbon-silicon skeleton are 598(1), 202(2), 239(3), 800(3) cm.$^{-1}$ where the numbers in brackets represent the numbers of fundamental frequencies of the value given. Thus the entropy obtained for a single fundamental frequency of 202 cm.$^{-1}$ must be multiplied by two. The fundamental frequencies due to vibration within a methyl group are 1264(1), 1427(2), 2905(1), 2963(2) cm.$^{-1}$ There are four times this number of vibrations counting all methyl groups. Finally, there are eight modes of vibration in which methyl groups rock without changing their internal configuration. The fundamental frequencies due to these modes are missing from the Raman and infra-red spectra, but by analogy with other molecules we can guess that they are about 950 cm.$^{-1}$ Thus we have forty-one modes of vibration or vibrational degrees of freedom; in addition there are three translational and seven rota-

TABLE XI

THE ENTROPY OF SILICON TETRAMETHYL AT THE BOILING POINT (299.81° K) ASSUMING FREE ROTATION

	Entropy Cal./Deg./Mole
Translational (From equation (44.3)) $=$	39.37
$\tfrac{7}{2} \times 4.575 \times \log 299.81 =$	39.66
$\tfrac{1}{2} \times 4.575 \times \log 162.4 \times 10^{-272} =$	−617.10
$4 \times 1.9869 \times 45.292 =$	359.84
$134.687 \times 1.9869 =$	267.60
$- 4.575 \log 972 =$	−13.67
$S_{t+r} =$	75.70
$S_v =$	12.00
	87.70

tional degrees of freedom making a total of fifty-one. This accounts for the three degrees of freedom for each of the seventeen atoms of the molecule and therefore all degrees of freedom have been included.

The calculation is summarized in Table XI.

(53) **Experimental Tests of the Assumption of Free Rotation**: A test of the assumption of free rotation of groups in organic molecules, that are not obviously sterically hindered, can be made by computing the entropy of the substance in the ideal gas state as outlined in the previous paragraph and comparing the result with that obtained using the third law of thermodynamics. Table XII summarizes the results obtained for a number of substances; except for methyl alcohol, the comparisons are made at the normal boiling point given in Column 2. Column 3 gives the difference $(S_f' - S_c)$ between the "spectroscopic" entropy (S_f') calculated on the assumption of free internal rotation without neglecting interaction and the "calorimetric" entropy (S_c) from heat capacity data down to 12° K.

TABLE XII

COMPARISON OF "CALORIMETRIC" AND "SPECTROSCOPIC" ENTROPIES IN THE IDEAL
GAS STATE OF NON-RIGID POLYATOMIC MOLECULES

Compound	Temperature ° K	$(S_f' - S_c)$ Cal./Deg./Mole	Potentials (kcal.)	Reference
Methyl alcohol .	298.16	1.75	6.40	[a]
Tetramethylmethane	282.61	8.6	4.50 (4)	[b,c,e]
Ethane......	184.10	1.55	3.15 (1)	[d]
Methylamine... ...	266.84	1.64	3.00 (1)	[e]
Propane...........	231.04	3.4	3.30 (2)	[f]
Ethyl alcohol.......	351.50	3.2	3.00 (1)	[g]
			10.00 (1)	
Isopropyl alcohol....	355.50	4.2	3.40 (2)	[h]
			5.00 (1)	
Acetone...........	329.30	0.6	1.00 (2)	[h]
Dimethylamine.....	280.04	3.03	3.46 (2)	[i]
Dimethylacetylene...	291.00	−0.3	0.0	[j]
Silicon tetramethyl..	299.82	1.55	1.28 (4)	[k]

[a] Kassel, *J. Chem. Phys.*, **4**, 493 (1936).

[b] Aston and Messerly, *J. Am. Chem. Soc.*, **58**, 2354 (1936).

[c] Pitzer, *J. Chem. Phys.*, **5**, 473 (1937).

[d] Kemp and Pitzer, *J. Am. Chem. Soc.*, **59**, 276 (1937).

[e] Aston, Siller and Messerly, *ibid.*, **59**, 1743 (1937).

[f] Kemp and Egan, *ibid.*, **60**, 1521 (1938).

[g] Schumann and Aston, *J. Chem. Phys.*, **6**, 480 (1938).

[h] Schumann and Aston, *loc. cit.*, p. 485.

[i] Aston, Eidinoff and Forster, *J. Am. Chem. Soc.*, **61**, 1539 (1939).

[j] Osborne, Garner and Yost, *J. Chem. Phys.*, **8**, 131 (1940).

[k] Aston, Kennedy and Messerly, *J. Am. Chem. Soc.*, **63**, 2343 (1941).

Except for dimethyl acetylene, acetone and silicon tetramethyl the differences per rotating group are quite large compared with the estimated error

(the calorimetric entropies are accurate to about 0.15 cal./deg./mole). In the absence of other information one could not say whether the differences are to be attributed to randomness in the crystal, as was found for N_2O, CO, H_2O and H_2, or to potentials hindering internal rotation. In this connection it is noteworthy that the difference is zero for methyl chloride and methyl bromide (Table X) so that there was no randomness in these cases.

It is possible to distinguish between the two alternatives by reference to the equilibrium in a reaction involving one or more of these compounds where there is a change in the number of internally rotating groups. Knowing the equilibrium constant from direct measurement, and the heat of reaction from thermal measurements at some convenient temperature, the value of ΔS can be calculated from equations (1.3) and (1.4). This value of ΔS can be compared with the one obtained from the "calorimetric" entropies of the reactants and products or the one from the "spectroscopic" entropies calculated on the assumption of free internal rotation. Such comparisons have shown that the calorimetric data are correct and that potentials hindering internal rotation must be the cause of the differences in Table XII. In the next section we shall see how these potentials can be evaluated either from such differences as those in Table XII or from the measured heat capacities of the gaseous substances. Column 4 of Table XII gives the potentials calculated to give the best fit with the calorimetric data.

(54) The Rotational Partition Function of Molecules with Restricted Internal Rotation: As a first approximation, we shall assume that the rotational partition function is separable into that for external and that for internal rotations, i.e., that it can be written as in (51.13)

$$Q_r = (Q_{r\ ext.}) \prod_{i=1}^{i=s-3} (r_{rr})_i, \qquad (54.1)$$

where $(Q_{r\ ext.})$ is given by (41.2) and $(r_{rr})_i$ the partition function for the hindered rotation of each internal group.

The evaluation of r_{rr} was first carried out by Teller and Topley [1] for the restricted internal rotation in ethane and their procedure has been applied to other molecules directly by Pitzer.[2]

Consider, as a simple example, the hindered rotation of one of the methyl groups relative to the other in ethane, and suppose that a repulsive force between hydrogen atoms causes the repulsion, although this supposition is not essential to the argument. As one group performs a single complete revolution with respect to the other, there will be three equally spaced maxima in the potential energy and three equally spaced minima, one midway between each pair of maxima. A potential function fulfilling these conditions is

$$V = \tfrac{1}{2}V_0(1 - \cos 3\phi). \qquad (54.2)$$

[1] *J. Chem. Soc.*, 885 (1935).
[2] *J. Chem. Phys.*, **5**, 469 (1937).

This function is sinusoidal with minima at $\phi = 0$, $\phi = 2\pi/3$, $\phi = 4\pi/3$ and maxima at $\phi = \pi/3$, $\phi = \pi$, $\phi = 5\pi/3$. Because of the simplicity of this type of function and lack of any further specific knowledge, we choose it for further calculation. In the general case of n equal minima this function becomes

$$V = \tfrac{1}{2} V_0 (1 - \cos n\phi). \tag{54.3}$$

The wave equation for a rotor with such a potential function will yield the necessary energy levels; this equation is

$$\frac{\partial^2 \psi(\phi)}{\partial \phi^2} + \frac{8\pi^2 I_{\text{red.}}}{h^2} [E_r - \tfrac{1}{2} V_0 (1 - \cos n\phi)] \psi = 0. \tag{54.4}$$

Substituting $2x/n$ for ϕ, placing $M(x) \equiv \psi(\phi)$ and $\theta = 8\pi^2 I_{\text{red.}} V_0/n^2 h^2$ with

$$a_r = \frac{32\pi^2 I_{\text{red.}}}{n^2 h^2} (E_r - \tfrac{1}{2} V_0), \tag{54.5}$$

we obtain

$$\frac{\partial^2 M(x)}{\partial x^2} + (a_r + 2\theta \cos 2x) M = 0, \tag{54.6}$$

which is Mathieu's differential equation. This equation has physically significant values of M for certain *characteristic* values (eigenvalues) of a_r only, namely a_1, a_2, a_3, etc. From these values of a_r we calculate the corresponding values of E_r using equation (54.5). These values, E_1, E_2, E_3, etc. are the energy levels of the system. To obtain the partition function, these energy levels are substituted into equation (21.1). They are non-degenerate so that $p = 1$ for each level; thus,

$$r_{rr} = \sum_r e^{-E_r/kT}. \tag{54.7}$$

Provided all n minima are equivalent, values of E_r corresponding to wave functions of the proper symmetry are obtained by choosing only the even values of a_r. Wilson[1] has tabulated the even values of a_r up to seven levels for rounded values of θ from 0 to 40.

(55) **The Thermodynamic Functions for Molecules with Restricted Internal Rotation:** The energy, heat capacity and entropy due to restricted internal rotations are calculated by substituting the partition function into equations (34.7), (34.9) and (31.11). The values of the energy and heat capacity are given in Appendix II, Tables A and B. Instead of recording the entropy value the quantity tabulated is the difference between the entropy S_{rr} and that (S_f) calculated using the free rotational partition function, r_i, as given by equation (51.14) with σ'' equal to the number of equivalent minima. The values given in Table C of Appendix II, are thus the quantities $S_{rr} - S_f$, with

$$S_f = R(- 0.775 + \tfrac{1}{2} \ln T + \tfrac{1}{2} \ln I_{\text{red.}} \times 10^{40} - \ln n). \tag{55.1}$$

[1] *Chem. Rev.*, **27**, 17 (1940).

In the same way in Table D of Appendix II, instead of the free energy defined by

$$F_{rr}/T = - R \ln r_{rr}, \tag{55.2}$$

there are tabulated the values of $(F_f - F_{rr})/T$, where

$$- F_f/T = R(- 1.275 + \tfrac{1}{2} \ln T + \tfrac{1}{2} \ln I_{\text{red.}} \times 10^{40} - \ln n). \tag{55.3}$$

The significance and use of F/T is discussed in Section (57).

All values are tabulated as a function of V_0/RT and n^2/IV_0 with V_0 expressed in cal. per mole and $I_{\text{red.}}$ in c.g.s. units per molecule.

As an example of the method we shall use the entropy of isobutane at 298.15° K in the ideal gas state, as obtained from the calorimetric data down to 10° K and the third law, to evaluate the potentials hindering the internal rotation of methyl groups in isobutane.[1] The molecule is treated as rigid to obtain ABC, the product of external moments (about principal axes through the center of gravity) ($A = 181.8 \times 10^{-40}$, $B = C = 106.8 \times 10^{-40}$). The moments do not depend on the position of the methyl groups since these rotate about principal axes. Using equations (44.3) and (47.3) with $\sigma' = 3$ substituted for σ we obtain for the entropy due to translation and external rotation,

$$S_{t+r} = 15.18 + 4R \ln T. \tag{55.4}$$

At 298.15° K, this yields the value $S_{t+r} = 60.45$ cal./deg./mole. The modes of vibration due to the carbon skeleton in isobutane are 796 (1), 967 (2), 372 (1), 436 (2) cm.$^{-1}$. The internal modes of vibration for each methyl group are 2900 (3), 1355 (1), 1453 (2), while those due to the single hydrogen on the carbon atom are 2900 (1), 1167 (2) cm.$^{-1}$. The number in brackets after each frequency gives the corresponding number of modes. The six modes of vibration in which methyl groups rock without changing their internal configuration are each given the average value 950 cm.$^{-1}$ by analogy with other molecules. The vibrational entropy at 298.15° K is then found to be 4.14 cal./deg./mole. The total entropy for translation, external rotation, and vibration is then 64.59. The six degrees of freedom of rotation and translation together with the thirty-three of vibration total thirty-nine. The fourteen atoms require forty-two degrees of freedom leaving three for the three internal rotations of the methyl groups. The "calorimetric" entropy is 70.43, so that 5.85 cal./deg./mole are due to the rotations of three methyl groups, i.e., 1.95 for each. The reduced moment $I_{\text{red.}}$ is found to be 5.2×10^{-40} g.cm.^{2}; hence, by equation (55.1) (with $n = 3$) we obtain 3.59 for S_f, and $S_f - S_{rr}$ is thus 1.64 cal./deg./mole. The hindering potential to produce this value of $S_f - S_{rr}$ is found from Table C of Appendix II, to be 3.87 kcal. per mole.

The potentials given in column 4 of Table XII have been obtained by the method outlined for isobutane. In cases where there is more than one kind of internally rotating group present in the molecule, the potentials hindering all

[1] See Aston, Kennedy and Schumann, *J. Am. Chem. Soc.*, **62**, 2059 (1940).

except one kind of group were estimated by analogy with other molecules. The contribution of these groups to the entropy was then calculated and added to that of all the other degrees of freedom except the internal rotation whose potential was to be evaluated. Subtracting this total from the calorimetric entropy gave the entropy due to the group (or like groups) whose potential could then be evaluated just as it was for the methyl groups in isobutane. For example, in the case of isopropyl alcohol the potential due to the methyl groups was taken to be between the values in propane (3.30 kcal.) and in isobutane (3.87 kcal.) and given the value 3.4 kcal. On this basis, information was available to calculate all but the entropy contribution of the OH group. To obtain agreement with the calorimetric entropy it was necessary to take the potential hindering the internal rotation of the OH groups as 5 kcal. When potentials are thus determined to fit the calorimetric data and then used to calculate thermodynamic functions at higher temperature any error due to estimated (or guessed) frequencies in the vibration spectrum is largely eliminated.

It is evident that if the vibration spectrum and moments of inertia are known for a polyatomic molecule with hindered internal rotations, it is possible to evaluate the hindering potentials from the measured gaseous specific heats corrected to the ideal gas states. To do this the heat capacity contributions due to all the degrees of freedom except the internal rotations are computed. The total is subtracted from the corrected measured heat capacity to obtain the contribution due to the hindered internal rotations. Using the appropriate reduced moments for the internal rotations the potentials can then be obtained from Pitzer's tables. In this way Kistiakowsky and co-workers have obtained the hindering potentials for certain molecules. Some typical results thus obtained are summarized in Table XIII. The first two values are in excellent agreement with the values in Table XII.

TABLE XIII
POTENTIALS HINDERING INTERNAL ROTATIONS FROM GASEOUS HEAT CAPACITIES

	V	Reference
Ethane	2.75 kcal.	a
Propane	3.40	b
Propylene	2.12	c
Dimethyl acetylene	<0.50	d

[a] Kistiakowsky, Lacher and Stitt, *J. Chem. Phys.*, **7**, 289 (1939).

[b] Kistiakowsky, Lacher and Ransom, *ibid.*, **6**, 900 (1938).

[c] Crawford, Kistiakowsky, Rice, Wells and Wilson, *J. Am. Chem. Soc.*, **61**, 2980 (1939).

[d] Crawford and Rice, *J. Chem. Phys.*, **7**, 437 (1939).

Another verification of the potentials in Table XII is obtained by employing the thermodynamic functions, calculated using the methods already described for compounds with restricted internal rotations, to calculate the equilibrium constant in a chemical reaction. The value thus obtained is compared with the measured value. Details of the method are given in paragraph (58).

For the comparison to be significant, the number of internal rotations must change during the reaction: four such comparisons are shown in Table XIV.

The case of n unequal minima would be extremely complicated to solve exactly; to obtain an approximate solution the method just outlined is assumed to be applicable. However, the considerations that led to the term $- R \ln n$ in equation (55.1) started with the postulate that n was the number of equally spaced equal minima and that this was an indication of an n-fold axis of symmetry. If all n minima are not equal, no rotations produce interchanges of identical atoms so that $- R \ln n$ is replaced by $- R \ln 1 = 0$ and this term drops out. Thus the entropy calculated by adding equation (55.1) to $S - S_f$ is $R \ln n$ greater, as it should be, than if the n minima were equal. In determining the $S - S_f$ values for the tables, both S and S_f were originally calculated assuming equal minima. Therefore S, as obtained by summing over the energy states, was also $R \ln n$ units smaller than if the minima were unequal because of the reduction of the number of states to meet symmetry requirements. It is perhaps the approximate method of solution which causes the barrier for ethyl alcohol to appear to be as high as 10 kcal. (cf. Table XII).

There remains to be considered the important case where V_0 is large. This case is of interest because if V_0 is sufficiently large there are only a small number of molecules in which the rotating group has sufficient energy to allow it to pass over the potential energy maximum. Consequently in most of the molecules the "rotating" group *cannot rotate* at all but oscillates about its position of minimum energy. In keeping with this the values of E_r and the eigenfunctions $M_r \equiv \psi_r(\phi)$ for low values of r are those of a harmonic oscillator. Consider the potential function

$$V = \tfrac{1}{2} V_0 [1 - \cos 3\phi]. \tag{55.5}$$

The force torque (F_ϕ) acting on the rotor at the angle ϕ from its equilibrium position is

$$F_\phi = \partial V / \partial \phi = \tfrac{1}{2} n V_0 \sin (n\phi). \tag{55.6}$$

For small displacements from the equilibrium position

$$\sin n\phi \cong n\phi$$
$$F_\phi = \tfrac{1}{2} n^2 V_0 \phi. \tag{55.7}$$

For a body executing simple angular harmonic oscillations

$$F_\phi = - k_\phi \phi \tag{55.8}$$

and the frequency is

$$\nu = \tfrac{1}{2}\pi \sqrt{\frac{k_\phi}{I_{\text{red.}}}} . \tag{55.9}$$

Hence, equation (55.7) represents a circular simple harmonic oscillation with

$$k = \tfrac{1}{2} n^2 V_0$$

TABLE XIV

MEASURED EQUILIBRIUM CONSTANTS IN CERTAIN GASEOUS REACTIONS COMPARED WITH THOSE CALCULATED USING THE HINDERING POTENTIALS GIVEN IN TABLE XII

Reaction	Equilibrium Constant (for pressures in atmospheres)							
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
$C_2H_6 = C_2H_4 + H_2$ [a]	(673° K.) 12530.	12000.	(773° K.) 465.	420.	(873° K.) 36.6	32.2	(973° K.) 4.8	5.0
$CO + 2H_2 = CH_3OH$ [b]	(473° K.) 0.0182	0.0182	(522.8° K.) 0.00182	0.00174	(578° K.) 0.000229	0.000324	(676° K.) 0.0000123	0.0000113
$C_2H_4 + H_2O = C_2H_5OH$ [c]	(383° K.) 0.0832	0.0676	(447° K.) 0.0380	0.0348	(517.5° K.) 0.00617	0.00631	(597.2° K.) 0.00166	0.00195
$(CH_3)_2CHOH = (CH_3)_2CO + H_2$ [d]	(450° K.) 0.46	0.27	(500° K.) 2.33	1.54				

[a] Smith and Vaughan, *J. Chem. Phys.*, **3**, 341 (1935); Teller and Topley, *J. Chem. Soc.*, 876 (1935); Kemp and Pitzer, *J. Am. Chem. Soc.*, **59**, 276 (1937); Pease and Byers, *ibid.*, **60**, 2489 (1938); Guggenheim, *Trans. Faraday Soc.*, **37**, 97 (1941).
[b] Kassel, *J. Chem. Phys.*, **4**, 493 (1936).
[c] Schumann and Aston, *ibid.*, **6**, 480 (1938).
[d] *Idem*, *ibid.*, **6**, 485 (1938).

and

$$\nu_0 = \tfrac{1}{2}\pi \sqrt{\frac{n^2 V_0}{2I_{\text{red.}}}} = \tfrac{1}{2}n\pi \sqrt{\frac{V_0}{2I_{\text{red.}}}} \qquad (55.10)$$

and energy levels

$$\epsilon_v = (v + \tfrac{1}{2})h\nu_0. \qquad (55.11)$$

Thermodynamic functions for this case can be obtained from the tables in Appendix 1. For the case of n equal minima there is no longer any necessity to introduce a term $-R \ln n$. This is because only the vibration occurring about one of the n positions of minimum energy is considered; the number of states is thus automatically reduced by the factor $1/n$.

It should be noted that if all n minima are not equivalent, isomeric compounds arise. In any one of the positions of minimum energy about which harmonic oscillation can occur the molecule has definite external moments and a definite vibration spectrum for all the other internal modes. In some other position of minimum energy these quantities, in general, will not be the same because the minima are not equal; and distinct molecular forms will arise. An experimental illustration of this fact is provided by the vibration spectrum of n-butane.[1] This molecule has unequal minima in the potential function for the relative internal rotation of the two ethyl groups about the central bond. The Raman spectrum and infra-red absorption spectrum show lines due to both forms; as a general rule, these forms will be in equilibrium.

The frequency ν_0, given by (55.10), is different for the vibrations about the non-equivalent positions of minimum energy. The forms of the molecule in these different positions must be considered as separate chemical species and the entropy of each species computed separately. To obtain the entropy of the equilibrium mixture the entropy of mixing of the species must be added. Such a situation has been discussed by Pitzer[2] for the case of n-butane. Unfortunately it is not possible to evaluate all the constants for the two forms made possible by the non-equivalent minima. If $S_{rr} - S_f$ is added to (55.1) to obtain the entropy due to the restricted internal rotation, in each of the forms, the term $-R \ln n$ must be included in (55.1). This allows for the fact that only $1/n$ of a revolution is considered.

(56) **Rigorous Treatment of Restricted Internal Rotation for Symmetrical Groups Attached to a Rigid Frame:** In case the potential is small, the interaction between internal and external rotation may be significant when the external moment is small. Crawford[3] has discussed the problem, in detail, where several symmetrical tops, such as methyl groups, are attached to a rigid frame. This situation corresponds to that for which a partition function has already been derived when the internal rotation is free (equation 51.11). Examples are methylamine, methyl alcohol, dimethyl ether, etc. (but not ethyl alcohol).

---

[1] Kohlrausch and Köppl, *Z. physik. Chem.*, **B, 26**, 209 (1934).

[2] *J. Chem. Phys.*, **5**, 473 (1937).

[3] *Ibid.*, **8**, 273 (1940).

The potential function assumed for the hindered rotations is that given by equation (54.3); however, the wave equation is applied to the whole molecule to obtain the energy levels. The results for a single internal rotor are:

$$S_{rr} = R[\ln G + (H/G)], \tag{56.1}$$

$$F_{rr}/T = R[(V_0/2RT) - \ln G], \tag{56.2}$$

$$E_{rr}/T = R[(V_0/2RT) + (H/G)], \tag{56.3}$$

$$C_{rr} = R[(J/G) - (H/G)^2], \tag{56.4}$$

which must be added to the values for external rotation, with

$$G = (\Omega^{1/2}G_R + G_V), \qquad H = (\Omega^{1/2}H_R + H_V), \tag{56.5}$$

$$J = \Omega^{1/2}J_R + J_V \tag{56.6}$$

and

$$G_V = \sum_V e^{-Y_r}; \qquad G_R = \sum_R e^{-\Omega Y_r}, \tag{56.7}$$

$$H_V = \sum_V Y_r e^{-Y_r}; \qquad H_R = \sum_R \Omega Y_r e^{-\Omega Y_r}, \tag{56.8}$$

$$J_V = \sum_V Y_r^2 e^{-Y_r}; \qquad J_R = \sum_R \Omega^2 Y_r^2 e^{-\Omega Y_r} \tag{56.9}$$

if $\Omega \simeq 0.5$ (i.e., invalid for methyl alcohol) where

$$Y_r = (n^2 h^2/32\pi^2 D\Omega RT)a_r, \tag{56.10}$$

$$\Omega = 1 - D[(\lambda_A^2/A) + (\lambda_B^2/B) + (\lambda_C^2/C)]. \tag{56.11}$$

As usual A, B and C are the principal moments of inertia of the whole molecule, D is the moment of inertia, about its axis, of the symmetrical group under consideration, λ_A, λ_B and λ_C are the cosines of the angles between the group axis and the principal axis, n is the number of minima of depth V_0. The a_r are the characteristic values of equation (54.6) with $D\Omega$ in place of $I_{\text{red.}}$; the lower values of a_r correspond roughly to vibrational levels and the upper ones to rotational levels. Lines drawn across Wilson's table indicate roughly the point of transition.[1] The sums over V are to be taken over the vibrational type of levels only, and the sums over R are to be taken over the rotational levels only. The values of a_r tabulated by Wilson have the correct symmetry properties for cases where n is the symmetry number of the rotating group. Where this latter condition is not fulfilled, the minima would probably not be equal in any case and the treatment would not apply.

Convenient tables of the quantities involved in the calculation are given in Appendix III.

---

[1] E. B. Wilson, Jr., *Chem. Rev.*, **27**, 17 (1940).

(57) The Heat Content and Free Energy from Statistical Mechanics: We shall consider as the heat content, the difference in heat content of a compound at the temperature in question, H, and at the absolute zero (H_0). For perfect gases H_0 is equal to E_0, the energy at the absolute zero, while for solids and liquids this is approximately true; hence we shall use $(H - E_0)$. For ideal gases and solids and liquids in their standard state this is denoted by $(H^0 - E_0^0)$. For gases,

$$(H^0 - E_0^0) = \int_0^T C_p^0 dT = (E^0 - E_0^0) + RT, \tag{57.1}$$

while for solids and liquids far below the critical temperature

$$(H^0 - E_0^0) \approx (E^0 - E_0^0). \tag{57.2}$$

The free energy, F^0, and the entropy, S^0, for gases, refer to the ideal gas state at 1 atm. pressure and for solids and liquids to the pure substance at unit activity; these quantities are related by

$$F^0/T = H^0/T - S^0, \tag{57.3}$$

so that,

$$(F^0 - E_0^0)/T = (H^0 - E_0^0)/T - S^0. \tag{57.4}$$

Consideration of the terms $(H^0 - E_0^0)/T$ and S^0 makes it possible to write down expressions for $(F^0 - E_0^0)/T$ corresponding to the various types of degree of freedom. The general expression in terms of the partition function is

$$-\left(\frac{F^0 - E_0^0}{T}\right) = R \ln \frac{Q_{tot.}}{N},$$
$$= R \ln \left(\frac{Q_t}{N} Q_{int.}\right). \tag{57.5}$$

For the three translational degrees of freedom of a perfect gas

$$-\left(\frac{F^0 - E_0^0}{T}\right)_t = \tfrac{5}{2} R \ln T + \tfrac{3}{2} R \ln m$$
$$- R \ln P + R \ln \left(\frac{(2\pi)^{3/2} k^{5/2}}{h^3}\right) \tag{57.6}$$

or

$$-\left(\frac{F^0 - E_0^0}{T}\right)_t = R[\tfrac{5}{2} \ln T + \tfrac{3}{2} \ln M - \ln P - 3.664]. \tag{57.7}$$

For the two classically excited rotational degrees of freedom of a diatomic molecule

$$-\left(\frac{F^0 - E_0^c}{T}\right)_r = -\left(\frac{F}{T}\right)_r = R \ln \left[\frac{8\pi^2 I k T}{h^2 \sigma}\right] \tag{57.8}$$

or

$$-\left(\frac{F^0 - E_0^0}{T}\right)_r = -\left(\frac{F}{T}\right)_r = R(\ln IT - \ln \sigma + 88.408). \quad (57.9)$$

For the three classically excited rotational degrees of freedom of a polyatomic molecule

$$-\left(\frac{F^0 - E_0^0}{T}\right)_r = -\left(\frac{F}{T}\right)_r = R \ln \frac{8\pi^2}{\sigma h^3} (8\pi^3 ABC)^{1/2}(kT)^{3/2} \quad (57.10)$$

or

$$-\left(\frac{F^0 - E_0^0}{T}\right)_r = -\left(\frac{F}{T}\right)_r$$
$$= R(3\tfrac{1}{2} \ln T + \tfrac{1}{2} \ln ABC - \ln \sigma + 133.186). \quad (57.11)$$

For a vibrational degree of freedom

$$-\left(\frac{F^0 - E_0^0}{T}\right)_v = -\left(\frac{F - E_0}{T}\right)_v = -R \ln (1 - e^{-x}), \quad (57.12)$$

in which $x = hc\nu_0/kT$ (ν_0 in cm.$^{-1}$). This quantity is tabulated in Appendix I. For the $3N$ elastic modes of a monatomic solid the corresponding expression is given in Table C of Appendix IV. For a classically excited free internal rotation where there is no interaction with the external rotations of the polyatomic molecule

$$-\left(\frac{F^0 - E_0^0}{T}\right)_f = -\left(\frac{F}{T}\right)_f = R \ln (2\pi)^{3/2}(kT)^{1/2}I_{\text{red.}}^{1/2}/h - R \ln n, \quad (57.13)$$
$$= R(- 1.275 + \tfrac{1}{2} \ln T + \tfrac{1}{2} \ln I_{\text{red.}} \times 10^{40} - \ln n), \quad (57.14)$$

where n is the number of equivalent positions of the rotor and $I_{\text{red.}}$ has the significance defined already.

If the rotation is hindered and the potential function is given by equation (54.3)

$$-\left(\frac{F^0 - E_0^0}{T}\right)_{rr} = -\left(\frac{F}{T}\right)_{rr} = -\left(\frac{F}{T}\right)_f - \left(\frac{F_{rr} - F_f}{T}\right), \quad (57.15)$$

where the last term on the right, tabulated in Appendix II, represents the difference between the true quantity and that for free rotation while the first term is calculated from (57.14). For s rotational degrees of freedom of which three are the external rotations and the remaining $(s - 3)$ are completely free rotations of rigid groups about an axis of symmetry attached to a rigid frame

$$-\left(\frac{F^0 - E_0^0}{T}\right)_r = -\left(\frac{F}{T}\right)_r = R \ln \frac{1}{\sigma}\left(\frac{2\pi kT}{h^2}\right)^{s/2}$$
$$\times 8\pi^2(2\pi)^{s-3}[K_1 K_2 \cdots K_{s-3}\Omega]^{1/2}, \quad (57.16)$$

where $K_1 K_2$ and K_{s-3} and Ω have the significance given for equation (51.11). In case the groups which rotate freely are non-rigid we must replace equation (57.16) by

$$-\left(\frac{F^0 - E_0^0}{T}\right)_r = -\left(\frac{F}{T}\right)_r = R \ln Q_r \qquad (57.17)$$

with Q_r given by (51.8). If asymmetrical groups are attached to a rigid frame we must also use equation (57.17).

The total $(F^0 - E_0^0)/T$ is obtained for the molecule by adding the contributions for all the external and internal degrees of freedom. Table XV gives the value of $-(F^0 - E_0^0)/T$ for a number of the simpler gases. In most cases equation (57.5) was used to calculate the translational, rotational and vibrational contribution. The values for graphite were obtained from the experimental heat capacities down to low temperatures.

(58) **The Calculation of Equilibrium Constants**: For a chemical reaction

$$aA + bB + \cdots = mM + nN + \cdots$$
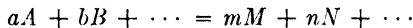
$$\Delta F^0 = \Delta E_0^0 + \Delta \left(\frac{F^0 - E_0^0}{T}\right) T, \qquad (58.1)$$

where ΔE_0^0 is the energy change in the reaction at the absolute zero and

$$\Delta \left(\frac{F^0 - E_0^0}{T}\right) = m \left(\frac{F^0 - E_0^0}{T}\right)_M$$
$$+ n \left(\frac{F^0 - E_0^0}{T}\right)_N - \cdots a \left(\frac{F^0 - E_0^0}{T}\right)_A - b \left(\frac{F^0 - E_0^0}{T}\right)_B \cdots, \quad (58.2)$$

where the bracketed quantities with the subscripts A, B, $\cdots$, M, N, $\cdots$, etc. are the total $(F^0 - E_0^0)/T$ values respectively for the reactants and products.

The quantity ΔE_0^0 can be obtained from the ΔH^0 of the reaction using the relation

$$\Delta H^0 = \Delta E_0^0 + \Delta(H^0 - E_0^0), \qquad (58.3)$$

where

$$\Delta(H^0 - E_0^0) = m(H^0 - E_0^0)_M + n(H^0 - E_0^0)_N$$
$$- \cdots a(H^0 - E_0^0)_A - b(H^0 - E_0^0)_B \cdots. \quad (58.4)$$

Inasmuch as $\Delta(H^0 - E_0^0)$ and $\Delta(F^0 - E_0^0)/T$ can be calculated if the complete mechanical behavior of the molecules of a system is known, it is evident that equation (58.1) can be used to calculate the equilibria in a chemical reaction when the heat of reaction is known. We shall illustrate the method by computing

$$\Delta F^0 = - RT \ln K_{atm}. \qquad (58.5)$$

for the reaction

$$C(\text{graphite}) + \tfrac{1}{2}O_2 \text{ (g.)} = CO \text{ (g.)} \quad \Delta H^0_{298.16} = -26,407 \text{ cal./mole,}$$
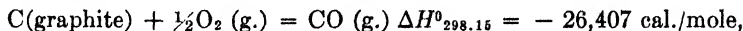
where $\Delta H^0{}_{298.15}$ is taken from the data of Rossini and co-workers.[1] The value of $H^0 - E_0{}^0$ for CO is 2070.9 cal. per mole at 298.15° K while for oxygen and graphite the values are 1035.2 cal. for half a mole and 251.4 cal. per atom respectively.[2] Thus $\Delta(H^0 - E_0{}^0) = 783.3$ cal. and $\Delta E_0{}^0 = -26,407 - 783 = -27,190$ cal. By adding this value divided by 298.15° K to the value of $\Delta(F^0 - E_0{}^0)/T$ at 298.15° K we obtain $\Delta F^0/T$ at 298.15° K. The value of $\Delta(F^0 - E_0{}^0)/T$ obtained from Table XV is -18.776 and $\Delta E_0{}^0/298.15$ is -91.13, so that $\Delta F^0/T$ is -109.91 cal. per degree. It follows, therefore, that

$$K_{\text{atm.}} = p_{CO}/p_{O_2}{}^{1/2} = 1.0 \times 10^{24}.$$

If $E_0{}^0$ for the elements is taken as zero, we may define quantities for compounds

$$F^0 = (F^0 - E_0{}^0) + \Delta E_0{}^0, \tag{58.6}$$

$$H^0 = (H^0 - E_0{}^0) + \Delta E_0{}^0, \tag{58.7}$$

where $\Delta E_0{}^0$ is the energy of formation at the absolute zero. The quantities defined by equations (58.6) and (58.7) may be called the free energy and heat content of a compound and are the quantities tabulated by Rodebush.[3] They refer to the process: elements in standard states at 0° K → compound in standard state at T° K. These quantities may be used like ΔF^0 and ΔH^0 of formation to compute free energy and heat content changes for a chemical reaction. The only difference is that whereas in using ΔF^0 and ΔH^0 the values for the elements are always zero, the F^0 and H^0 values for the elements are *not* zero but respectively equal to the $(F^0 - E_0{}^0)$ and $(H^0 - E_0{}^0)$ values that we have previously considered. These quantities are particularly convenient for computing free energies and equilibrium constants in reactions involving organic compounds; $\Delta E_0{}^0$ is then obtained from the heat of combustion.

(59) **The Chemical Constants:** We have just described a method which is sufficient to calculate the equilibrium constants of chemical reactions from thermal data alone. This is based on the third law of thermodynamics, but sometimes the system proposed by Nernst is used. The two methods differ considerably in formal development but the *exact* application of Nernst's method is equivalent to the one just treated.

Consider a chemical reaction involving the chemical compounds A, B, $\cdots$, M, N, etc.

$$a\text{A} + b\text{B} + \cdots = m\text{M} + n\text{N} + \cdots.$$
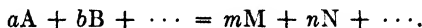
For this reaction

$$\ln K = -\frac{\Delta F^0}{RT} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}, \tag{59.1}$$

[1] Rossini, *J. Res. Nat. Bur. Stand.*, 6, 37 (1931). Rossini and Jessup, *ibid.*, 21, 491 (1938.)

[2] Clayton and Giaque, *J. Am. Chem. Soc.*, 54, 2623 (1932).

[3] Rodebush and Rodebush, International Critical Tables, Vol. 5, page 89 (1929).

TABLE XV

The Functions S^0 and $\left(\dfrac{F^0 - E_0^0}{T}\right)$ in Calories per Degree per Mole for Substances in the Ideal Gas State and Graphite (Nuclear Spin Not Included)

Substance	Refer-ence	Temperature, °K							
		298.15	300	400	600	800	1000	1200	1500
S^0	a	31.230	31.269	33.267	36.101	38.115	39.721	41.053	42.739
$H_2 - \left(\dfrac{F^0 - E_0^0}{T}\right)$	b	24.436	24.480	26.438	29.218	31.204	32.752	34.027	35.605
S^0	c	49.018	—	51.121	54.117	56.381	58.214	—	61.680
$O_2 - \left(\dfrac{F^0 - E_0^0}{T}\right)$	c	42.081	42.125	44.127	46.984	49.062	50.715	52.095	53.826
$Cl_2 - \left(\dfrac{F^0 - E_0^0}{T}\right)$	d	45.951	45.997	48.148	51.298	53.614	55.453	56.979	58.876
S^0	e	45.788	45.828	47.833	50.701	52.815	54.527	—	57.807
$N_2 - \left(\dfrac{F^0 - E_0^0}{T}\right)$	f	38.834	38.876	40.877	43.705	45.729	47.322	48.646	50.301
$HCl - \left(\dfrac{F^0 - E_0^0}{T}\right)$	g	37.734	37.778	39.771	42.588	44.597	46.171	47.472	49.096
S^0	h	45.101	45.151	47.472	50.864	53.425	55.542	57.380	59.783
$H_2O - \left(\dfrac{F^0 - E_0^0}{T}\right)$	h	37.179	37.230	39.513	42.765	45.121	46.999	48.579	50.586
$CH_4 - \left(\dfrac{F^0 - E_0^0}{T}\right)$	i	—	36.654	39.006	42.546	45.372	47.826	50.035	53.026
S^0	j		47.357	49.366	52.254	54.396	56.133	—	59.455
$CO - \left(\dfrac{F^0 - E_0^0}{T}\right)$	k	40.364	40.408	42.408	45.238	47.271	48.876	50.210	51.880
S^0	l	—	51.140	53.842	58.141	61.543	64.370	66.787	69.917
$CO_2 - \left(\dfrac{F^0 - E_0^0}{T}\right)$	l	—	43.620	45.848	49.261	51.921	54.137	56.049	58.513
S^0	m	50.350	51.494	52.449	55.408	57.607	59.392	—	62.780
$NO - \left(\dfrac{F^0 - E_0^0}{T}\right)$	m	42.985	43.033	45.141	48.100	50.314	51.878	53.259	54.979
Graph-ite $- \left(\dfrac{F^0 - E_0^0}{T}\right)$	n	0.545	0.551	0.854	1.510	2.164	2.798	3.391	4.206
S^0	o	56.84	—	60.19	65.24	69.08	72.16	74.74	77.97
$CS_2 - \left(\dfrac{F^0 - E_0^0}{T}\right)$	o	48.28	—	50.90	54.89	57.97	60.51	62.67	65.44
S^0	p	49.151	—	51.58	55.14	57.92	60.25	62.29	64.92
$H_2S - \left(\dfrac{F^0 - E_0^0}{T}\right)$	p	41.174	—	43.53	46.83	49.27	51.24	52.92	55.06

where ΔH^0 and ΔS^0 are the heat of reaction and entropy changes for the substances in their standard states; hence

$$\ln K = -\frac{\Delta H^0}{RT} + \frac{(mS_M^0 + nS_N^0 + \cdots - aS_A^0 - bS_B^0)}{R}, \qquad (59.2)$$

where S_A^0, S_B^0, etc. are the entropies of the chemical substances involved in the chemical reaction in their standard states. From the relationship

$$\frac{\partial S^0}{\partial T} = \frac{C_p^0}{T}, \qquad (59.3)$$

integration gives

$$S_A^0 = \int \frac{C_p^0}{T} dT + I_A, \qquad (59.4)$$

where the integral is an indefinite one and I_A is constant; hence from (59.2)

$$\ln K = -\frac{\Delta H^0}{RT} + \frac{1}{R}\int \frac{\Delta C_p^0}{T} dT + \frac{(mI_M + nI_N \cdots - aI_A - bI_B)}{R}. \qquad (59.5)$$

This equation can be written

$$\ln K = -\frac{\Delta H^0}{RT} + \frac{1}{R}\int \frac{\Delta C_p^0}{T} dT + i_R, \qquad (59.6)$$

where

$$Ri_R = I_R = mI_M + nI_N \cdots - aI_A - bI_B. \qquad (59.7)$$

It is quite evident that the constant in equation (59.6) $(i_R = I_R/R)$ needs to be known before the equation can be used to calculate the equilibrium constant

[a] Davis and Johnston, *J. Am. Chem. Soc.*, **56**, 1045 (1934).

[b] Giauque, *ibid.*, **52**, 4816 (1930).

[c] Johnston and Walker, *ibid.*, **55**, 172 (1933).

[d] Giauque and Overstreet, *ibid.*, **54**, 1731 (1932).

[e] Johnston and Davis, *ibid.*, **56**, 271 (1934).

[f] Giauque and Clayton, *ibid.*, **55**, 4875 (1933).

[g] Giauque and Overstreet, *ibid.*, **54**, 1731 (1932). $S^0_{298.15} = 44.658$ cal./deg./mole.

[h] Gordon and Barnes, *J. Chem. Phys.*, **2**, 65,549 (1934).

[i] Kassel, *J. Am. Chem. Soc.*, **55**, 1357 (1933). Aston, unpublished. $S^0_{298.15} = 44.66$ cal./deg./mole.

[j] Johnston and Davis, *ibid.*, **56**, 271 (1934).

[k] Clayton and Giauque, *ibid.*, **55**, 5071 (1933).

[l] Kassel, *ibid.*, **56**, 1838 (1934).

[m] Johnston and Chapman, *ibid.*, **55**, 153 (1933).

[n] Clayton and Giauque, *ibid.*, **54**, 2610 (1932).

[o] Cross, *J. Chem. Phys.*, **3**, 825 (1935).

[p] Cross, *ibid.*, **3**, 168 (1935).

of a chemical reaction from thermal data alone, and this requires evaluation of I in equation (59.4) for each chemical substance.

For a crystalline solid

$$\int_0^T \frac{C_p{}^0}{T} dT = \left[\int \frac{C_p{}^0}{T} dT \right]_0^T = \int \frac{C_p{}^0}{T} dT, \qquad (59.8)$$

since C_p approaches zero asymptotically at the absolute zero and therefore at $T = 0$, $C_p/T = 0$ and the lower limit is zero: hence for the crystalline solid A

$$S_A = \int_0^T (C_p{}^0/T) dT + I_A \qquad (59.9)$$

and since the entropy of a perfect crystal is zero at the absolute zero I_A is zero for a perfect crystalline substance. It remains to evaluate I_A for gaseous substances.

Consider the reaction,
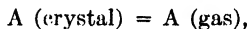
$$\text{A (crystal)} = \text{A (gas)},$$

involving a perfect crystal and apply equation (59.6) to it. In this case, K is simply the vapor pressure of the crystal; hence equation (59.6) becomes

$$\ln P_A = - \frac{\Delta H^0}{RT} + \frac{1}{R} \int \frac{\Delta C_p{}^0}{T} dT + i_A. \qquad (59.10)^*$$

Since $I_{A(\text{crystal})}$ for the perfect crystalline substance is zero.

$$i_A = I_{A(\text{gas})}/R. \qquad (59.11)$$

The problem of obtaining I_A is thus the same as that of evaluating i_A in equation (59.10).

Before continuing further with the problem in this form let us investigate the connection between equation (59.6) and the empirical expression for $\ln K$ based on the integrated free energy equation. To do this we substitute

$$\Delta H^0 = \Delta H_0{}^0 + \int_0^T \Delta C_p{}^0 dT \qquad (59.12)$$

---

* Strictly speaking P_A is the pressure of vapor in equilibrium with the crystal when the crystal is under a pressure of one atmosphere (unit activity) whereas the vapor pressure is the pressure of vapor in equilibrium with the crystal under its own vapor pressure. At vapor pressures of the order of 1 atm. the two are identical for practical purposes. Actually, Nernst obtained equation (59.10) from the approximate Clapeyron equation

$$\frac{d \ln P}{dT} = \frac{\Delta H}{RT^2}.$$

in equation (59.6) which gives

$$\ln K = -\frac{\Delta H_0^0}{RT} - \frac{1}{RT}\int_0^T \Delta C_p^0 dT + \frac{1}{R}\int \frac{\Delta C_p^0}{T} dT + i_R, \quad (59.13)$$

where ΔH_0^0 is the heat of reaction at the absolute zero. In (59.13) the first of the integrals is definite and the second indefinite, the lower limit of the former being zero. On introducing the upper limit and dividing by T, a constant term, r, is introduced if ΔC_p contains a constant term. If the definite integral is differentiated as a product and then reintegrated we obtain

$$-\frac{1}{RT}\int_0^T \Delta C_p^0 dT = -\frac{1}{R}\int d\left(\frac{1}{T}\int_0^T \Delta C_p^0 dT\right) + r$$

$$= \frac{1}{R}\int \frac{\left(\int_0^T \Delta C_p^0 dT\right) dT}{T^2} - \frac{1}{R}\int \frac{\Delta C_p^0}{T} dT + r. \quad (59.14)$$

Solving (59.14)

$$r = -\frac{1}{RT}\int_0^T \Delta C_p^0 dT - \frac{1}{R}\int \frac{\left(\int_0^T \Delta C_p^0 dT\right) dT}{T^2} + \frac{1}{R}\int \frac{\Delta C_p^0}{T} dT. \quad (59.15)$$

Substituting for the definite integral in (59.13) by use of (59.14)

$$\ln K = -\frac{\Delta H_0^0}{RT} + \frac{1}{R}\int \frac{\left(\int_0^T \Delta C_p^0 dT\right) dT}{T^2} + J, \quad (59.16)$$

in which

$$J = r + i_R \quad (59.17)$$

and r is determined by (59.15).

The equilibrium constant can be expressed as

$$\ln K = -\frac{\Delta F^0}{RT} = -\frac{\Delta H_0^0}{RT} + \frac{a_0}{R}\ln T$$

$$+ \frac{a_1}{2R}T + \frac{a_2}{2\times 3R}T^2 + \cdots + \frac{a_n T^n}{n(n+1)R} + \cdots + \frac{I}{R}. \quad (59.18)$$

The quantity ΔH_0^0 is the heat of reaction at the absolute zero if *and only if*

$$\Delta C_p = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + \cdots + a_n T^n + \cdots \quad (59.19)$$

expresses the difference in heat capacity for all values of T (i.e., ΔC_p can be expressed as a convergent power series in T by a MacLaurin expansion).

When (59.19) is convergent, equation (59.18) is identical with equation (59.16) and

$$I/R = r + i_R = r + I_R/R = J. \tag{59.20}$$

Thus the connection between the integration constant (I) of the usual free energy equation and i_R is readily seen.

Applying equation (59.16) to the process

$$A \text{ (crystal)} = A \text{ (gas)}$$

$$\ln P_A = -\frac{\Delta H_0^0}{RT} + \frac{1}{R} \int \frac{\left(\int_0^T \Delta C_p^0 dT \right) dT}{T^2} + j_A, \tag{59.21}$$

where ΔH_0^0 is the heat of vaporization at the absolute zero and

$$j_A = r_A + i_A. \tag{59.22}$$

r_A is the value of r obtained by applying (59.15) to the process of vaporization.

Suppose that the vapor pressure of the crystal can be represented by the equation

$$\ln P_A = -\frac{\Delta H_0^0}{RT} + b_0 \log T + b_1 T + b_2 T^2 + \cdots + b_n T^n + \text{const.} \tag{59.23}$$

If the last terms form a convergent power series in T and the equation is strictly true for all values of T, i.e., the equation is an analytic representation of $\ln P_A$, then *and only then*

$$\text{const.} = r_A + i_A = j_A. \tag{59.24}$$

The quantity j_A is termed the "true" chemical constant to distinguish it from the "conventional" chemical constant which is the constant of a formal and approximate equation like (59.23). It is to be noted that j_A is the constant of a perfectly exact equation, providing the pressures are lower than 1 atm.

Just as there is a simple relation between i_R and i_A, etc. so there is a simple connection between J and j_A. It has already been seen that the heat capacities of solids and the vibrational heat capacities of gases (including the part due to restricted rotation) are zero at the absolute zero. Therefore in a power expansion for these quantities the constant term is zero. Thus only the classical translational and rotational heat capacities of the gases *at constant pressure* contribute to r. Let $C_p(0)_A$, $C_p(0)_B$, $\cdots$, $C_p(0)_M$, $C_p(0)_N$ be these quantities which are the heat capacities of the gases at the absolute zero

$$r = -\frac{C_p(0)_M + C_p(0)_N \cdots - C_p(0)_A - C_p(0)_B}{R} = -\frac{\Delta C_p(0)}{R}. \tag{59.25}$$

* Values of T which lead to vapor pressures much greater than 1 atm. excepted.

Referring to equation (59.21) it is evident that

$$r_A = -\frac{C_p(0)_A}{R} \qquad (59.26)$$

and we see that

$$r = r_M + r_N \cdots - r_A - r_B \qquad (59.27)$$

or

$$J = j_M + j_N \cdots - j_A - j_B. \qquad (59.28)$$

Hence, r, and therefore also j, is zero for crystalline substances.

(60) **Vapor Pressure of Crystals at Low Temperatures—Theoretical Values of the Chemical Constants:** Let us apply equation (59.21) to a perfect crystal in equilibrium with its vapor under circumstances when the latter may be treated as a perfect gas with classically excited translation and rotation over all temperatures of interest. As the constant j will not change with temperature we shall find j for circumstances where the temperature is low and the heat capacity of the crystal, which is proportional to T^3, may be neglected. The temperature is also sufficiently low that we may neglect the vibrational heat capacity of the gas (proportional to $(\theta/T)^2 e^{-\theta/T}$). At the same time we consider that the gas continues to have classically excited translation and rotation. The fact that this situation is a hypothetical one makes no difference as it was devised simply to aid in evaluating the constant j_A of equation (59.21) which if carried to low temperatures on the basis of classical translational and rotational heat capacity applies to just such a situation.

In this case—

    (a) $\Delta C_p = 5R/2$ when the vapor is a monatomic gas

    (b) $\Delta C_p = 7R/2$ when the vapor is a diatomic gas or a linear rigid polyatomic molecule

    (c) $\Delta C_p = 8R/2$ when the vapor is a rigid nonlinear polyatomic molecule

    (d) $\Delta C_p = (s + 5)R/2$ when the vapor is a nonrigid polyatomic molecule with $(s - 3)$ internal free rotational degrees of freedom.

We shall not limit ourselves to the case where the crystal is perfect but consider the case where there may be a number of orientations (ω_0') of molecules in the crystal and there may be a number of quantum states (ω_0'') corresponding to the state of lowest energy in the crystal. This last situation may arise as a result of different orientations of the nuclear spins and electronic spins with the same energy. Let $\omega_0' \times \omega_0''$ be denoted by ω_0. The entropy of the crystal at the absolute zero is $R \ln \omega_0$. Moreover for each rotational state, in the gas, of a definite orientation (quantum numbers J and M) let there be v_0 states of essentially equal energy due to different orientations of the nuclear spins (*of equal energy*) and to the number of electronic states of lowest energy (i.e., for which $\Delta\epsilon_e/kT \to 0$).

(a) *Crystal yielding monatomic vapor:*
Applying equation (59.1) to the process

$$A \text{ (crystal)} = A \text{ (gas)}$$

$$\ln P = -\Delta H^0/RT + \Delta S^0/R, \tag{60.1}$$

where

$$\Delta S^0 = S^0_{(gas)} - S^0_{(crystal)}. \tag{60.2}$$

At low temperatures

$$S^0_{(crystal)} = R \ln \omega_0, \tag{60.3}$$

while $S^0_{(gas)}$, the entropy of the ideal gas at 1 atm., is given by the Sackur-Tetrode equation (32.13) with $P = 1$ and $p_s = v_0$. Since

$$\Delta H^0 = \Delta H_0^0 + \tfrac{5}{2}RT, \tag{60.4}$$

it follows that

$$\ln P = -\frac{\Delta H_0^0}{RT} + \tfrac{5}{2} \ln T + \ln \left(\frac{(2\pi m)^{3/2} k^{5/2} v_0}{h^3 \omega_0} \right). \tag{60.5}$$

Comparing (60.5) with (59.23) and (59.24)

$$j = \ln \left(\frac{(2\pi m)^{3/2} k^{5/2}}{h^3} \cdot \frac{v_0}{\omega_0} \right). \tag{60.6}$$

(b) *Crystal yielding diatomic vapor:*
The procedure is similar to the previous one and the entropy of the ideal gas is the sum of the translational entropy as given by equation (32.13) and the rotational entropy by equation (47.1).

$$\Delta H^0 = \Delta H_0^0 + \tfrac{7}{2}RT \tag{60.7}$$

and so

$$\ln P = -\frac{\Delta H_0^0}{RT} + \tfrac{7}{2} \ln T + \ln \left[\frac{(2\pi m)^{3/2} k^{5/2}}{h^3} \right] \\ + \ln \left(\frac{8\pi^2 I k}{\sigma h^2} \right) + \ln v_0 - \ln \omega \tag{60.8}$$

and

$$j = \ln \left[\frac{8\pi^2 I (2\pi m)^{3/2} k^{7/2}}{\sigma h^5} \cdot \frac{v_0}{\omega_0} \right]. \tag{60.9}$$

(c) *Crystal yielding rigid polyatomic vapor:*
By a procedure analogous to that for diatomic vapors,

$$j = \ln \left[\frac{8\pi^2 (8\pi^3 ABC)^{1/2} (2\pi m)^{3/2} k^{8/2}}{\sigma h^6} \cdot \frac{v_0}{\omega_0} \right]. \tag{60.10}$$

(d) *Crystal yielding vapor whose polyatomic molecules have $(s - 3)$ free internal rotational degrees of freedom:*

Using the same procedure and making use of equation (31.11) for the total rotational entropy,

$$j = \ln \left[\frac{(2\pi m)^{3/2} k^{5/2} v_0}{\omega_0 h^3} \cdot \frac{Q}{T^{s/2}} \right] \quad (60.11)$$

with Q given by (51.8), or

$$j = \ln \left[\frac{(2\pi m)^{3/2} k^{5/2} (2\pi k)^{s/2} 8\pi^2 \int_0^{2\pi} \cdots \int_0^{2\pi} [S]^{1/2} d\omega_1 \cdots d\omega_{S-3}}{\sigma h^{s+3}} \cdot \frac{v_0}{\omega_0} \right], \quad (60.12)$$

where σ is the number of equivalent positions which can be produced by both the external and internal rotations of the molecule. This expression is simplified when the special conditions apply which simplify the determinant $[S]$.

For the conditions to which the above values of j apply, equation (59.2) may be written

$$\ln P_A = -\frac{\Delta H_0^0}{RT} + \frac{s + 5}{2} R \ln T + \frac{1}{R} \int \frac{\left(\int_0^T C' dT \right) dT}{T^2}$$

$$- \frac{1}{R} \int \frac{\left(\int_0^T C_s dT \right)}{T^2} dT + j_A, \quad (60.13)$$

where C' is the part of the specific heat of the gas due to vibration and any restricted internal rotation and C_s is the heat capacity of the crystal. Here also s is the number of degrees of freedom of rotation which are entirely free.

For reactions in which all the gases have classical translation and rotation equation (59.16) may be written in the following form for practical purposes

$$\ln K = -\frac{\Delta H_0^0}{RT} + \frac{1}{R} \Delta C_p(0) \ln T + \frac{1}{R} \int \frac{\left(\int_0^T \Delta C' dT \right) dT}{T^2}$$

$$+ \frac{1}{R} \int \frac{\left(\int_0^T \Delta C_s dT \right) dT}{T^2} + J, \quad (60.14)$$

where $\Delta C_p(0)$ is the difference between the heat capacities at constant pressure of the gases on the right and left of the chemical equation *exclusive of the vibrational and restricted internal rotational contributions* and the first integral involves $\Delta C'$ which is the difference between the vibrational and restricted internal rotational contributions for the gases on the right and for the gases on the left. The second integral is the corresponding quantity for the total heat capacities of the solids. Evidently the quantity $\Delta C_p(0)/R$ is some integer times one half from its very nature.

<div align="center">

TABLE XVI *

CHEMICAL CONSTANTS OF GASES

</div>

Formula of Vapor	Electronic Normal State	$\dfrac{v_0}{\sigma\omega_0}$	Moment of Inertia $I \times 10^{40}$	j calc.	j obs.
Hg	^1S	1		1.866	1.83 ± 0.03 [1]
Cd	^1S	1		1.488	1.50 ± 0.07 [1,4]
Zn	^1S	1		1.135	1.21 ± 0.15 [7]
Pb	^1S	1		1.887	2.00 ± 0.3 [1,5]
Mg	^1S	1		0.49	0.47 ± 0.2 [7]
Ne	^1S	1		0.37	0.39 ± 0.04 [8]
A	^1S	1		0.813	0.79 ± 0.04 [1]
Na	^2S	$^2/_1$		0.756	0.78 ± 0.1 [2,3,6]
K	^2S	$^2/_1$		1.10	1.0 [2,3]
Tl	$^2P_{1/2}$	$^2/_1$		2.18	2.37 ± 0.3 [7]
H$_2$ ¼ Para	$^1\Sigma$	$(\tfrac13)^{3/4}\times\tfrac12$	0.463	-3.72	-3.68 ± 0.03 [9]
¾ Ortho	$^1\Sigma$		0.463		
N$_2$	$^1\Sigma$	$^1/_2$	13.8	-0.18	-0.16 ± 0.03 [9]
O$_2$	$^3\Sigma$	$^3/_2$	99.15	0.53	0.55 ± 0.02 [9]
HCl	$^1\Sigma$	$^1/_1$	2.765	-0.42	-0.40 ± 0.03 [9]
HBr	$^1\Sigma$	$^1/_1$	3.35	0.20	0.24 ± 0.04 [9]
HI	$^1\Sigma$	$^1/_1$	4.31	0.61	0.65 ± 0.05 [9]
Cl$_2$	$^1\Sigma$	$^1/_2$	116.	1.35	1.66 ± 0.08 [9]
Br$_2$	$^1\Sigma$	$^1/_2$	445.	2.47	2.59 ± 0.10 [9]
I$_2$	$^1\Sigma$	$^1/_2$	820.	3.03	3.08 ± 0.05 [9]
CO	$^1\Sigma$	$^1/_2$	15.0	-0.141	-0.07 ± 0.05 [9]
NH$_3$		$^1/_3$		-1.55	-1.50 ± 0.04 [9]
CH$_4$		$^1/_4$	5.3	-1.94	-1.97 ± 0.05 [9]

* Fowler, Statistical Mechanics, Cambridge University Press (1936), pages 218 and 223.
[1] Egerton, *Proc. Phys. Soc.*, **37**, 75 (1925).
[2] Edmonson and Egerton, *Proc. Roy. Soc.*, [A], **113**, 533 (1927).
[3] Zeidler, *Z. physik. Chem.*, **123**, 383-(1926).
[4] Lange and Simon, *ibid.*, **134**, 374 (1928).
[5] Harteck, *ibid.*, **134**, 1 (1928).
[6] Ladenburg and Thiele, *ibid.*, B, **7**, 161 (1930).
[7] Coleman and Egerton, *Phil. Trans. Roy. Soc.*, [A], **234**, 177 (1935).
[8] Clusius, *Z. physik. Chem.*, B, **4**, 1 (1929).
[9] Eucken, *Physik. Z.*, **31**, 361 (1930).

It is apparent that the entire right-hand sides of equations (60.13) and (60.14) omitting $-\Delta H_0^0/RT$ are exactly the quantity $-\Delta(F^0 - E_0^0)/T$, which we have discussed earlier, divided by R. Moreover, it can be seen readily that the chemical constants j_A etc. from which J is calculated are the constants in the expressions for $-(F^0 - E_0^0)_A/T$ etc. due to translation and rotation divided by R, and that the temperature dependent parts of these expressions are used in forming $\Delta C_p(0) \ln T$.

From the relation

$$\frac{\partial(F/T)}{\partial T} = -\frac{H}{T^2}, \qquad (60.15)$$

it is evident that the two integrals are differences between the quantities $-(F^0 - E_0^0)/T$ due to the vibrational degrees of freedom of the gases and for the solids respectively for the substances on the right and left of the chemical equation. Thus we see that the method of chemical constants is exactly equivalent to the earlier method but considerably more complicated.

The comparisons in Table X can be taken as a check of the accuracy of the method of chemical constants because the same principles are involved. However, it is evident from this table that although, in calculating vapor pressure, a chemical constant must be used with a value of ω_0 appropriate to the solid, in calculating equilibrium constants the factor in ω_0 due to random orientation must be omitted.

In Table XVI, column 5, are given calculated values of the chemical constants for certain gases named in column 1 whose normal electronic state is given in column 2; column 3 gives the value of v_0/ω used in the calculation, while column 4 gives the moment of inertia.

The chemical constants given in column 5 are those of equations (60.6) (60.9) and (60.10) divided by 2.303 so that they are constants for use in equations (60.13) and (60.14) rewritten in terms of the common logarithm. Column 6 gives observed values of the constants determined from the measured vapor pressures and equation (60.13). The agreement between the calculated and observed values of j is all that could be desired and constitutes an excellent confirmation of the third law. In the case of hydrogen ω_0 for the crystal is taken as $(4)^{1/4}(12)^{3/4}$. The quantity v_0/σ for the gas is taken as $\tfrac{4}{3}$. This is in accord with our previous discussion. Thus $v_0/\omega_0\sigma$ is equal to $(\tfrac{1}{3})^{3/4} \times \tfrac{1}{2}$. However, it is to be noted that before use in calculation of J the value of j_{H_2} must have $\tfrac{3}{4} \log 3$ added to it. The terms in $v_0/\omega_0\sigma$ are given explicitly except for the part due to nuclear spin which has been cancelled.

In Table XVII are given values of the constant J in equation (60.14) for certain gas reactions recorded in column 1. Column 2 gives the calculated values of J obtained from the chemical constants while column 3 gives the observed value obtained from equation (60.14), the equilibrium constant and the measured heats (or temperature coefficients of $\ln K$). The chemical constants used in deriving the results of column 2 were the calculated values in

TABLE XVII *

COMPARISON OF OBSERVED AND CALCULATED VALUES OF J

Reaction	J calc.	J obs.
$H_2 + Cl_2 = 2HCl$	1.17	1.12 ± 0.2 [1]
$H_2 + Br_2 = 2HBr$	1.29	1.25 ± 0.45 [1]
$H_2 + I_2 = 2HI$	1.55	1.51 ± 0.12 [1]
$2NO = N_2 + O_2$	-1.31	-0.95 ± 0.3 [1,2]

* Taken from Fowler, *op. cit.*, page 228.

[1] Eucken, *Physik. Z.*, **30**, 818 (1929).

[2] These values refer to high temperatures at which v_0 for NO is 4 and $j_{\text{calc.}}$ is 0.84, i.e., the energies of the levels $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ are considered equal.

column 5 of Table XVI with $R \ln \omega_0$ added to them. Because of the cancellation of nuclear spin effects the part of ω_0 due to nuclear spin is not included when calculating this term. The experimental data used for calculating the values in column 3 are not always all that could be desired from a modern point of view. The agreement between the observed and calculated values of J is a further confirmation of the third law.

(61) **The Energy and Heat Capacity of a Simple Monatomic Crystalline Solid:** Space will not permit a discussion of the early attempts to calculate the heat capacity of crystalline substances nor will it permit us to follow all the modern work.* We shall content ourselves by giving the theory for simple monatomic crystalline substances as originally formulated by Debye. Consider one mole of the crystal containing N atoms: we shall treat this crystal as an isotropic elastic solid whose elastic constants are λ and μ.[1] The velocities of the longitudinal waves (c_L) and transverse waves (c_T), as sound is propagated through the crystal, are given in terms of these elastic constants by

$$c_L = \sqrt{\frac{\lambda + 2\mu}{\rho}} \qquad \text{and} \qquad c_T = \sqrt{\frac{\mu}{\rho}}, \qquad (61.1)$$

where ρ is the density of the crystal.[2] When the crystal is in thermal motion there will be three sets of standing (acoustical) waves set up in the crystal, one of them longitudinal, in which the atoms move parallel to the direction of motion (say x direction), and two transverse at right angles (corresponding y and z directions). The former have the velocity c_L and the latter c_T. The number of modes of vibration with frequencies lying between ν and $\nu + d\nu$ is

$$dz = \frac{4\pi V \nu^2 d\nu}{c_L{}^3} + \frac{8\pi V \nu^2 d\nu}{c_T{}^3}, \qquad (61.2)$$

where V is the volume occupied by the crystal. The first term gives the number of longitudinal modes and the latter the number of transverse modes. The number of transverse waves is obviously twice that of the longitudinal waves since there are two sets of the latter to one of the former.[3]

It is seen from equation (43.7) that the average energy of a mode of vi-

---

* For a full discussion see Fowler, Statistical Mechanics, Cambridge University Press, 1936.

[1] See Haas, Introduction to Theoretical Physics, Vol. 1, page 176, Van Nostrand Co., New York, 1928. These two fundamental elastic constants are such that Young's modulus is $E = \mu(3\lambda + 2\mu)/(\lambda + \mu)$ and Poisson's ratio is $\eta = \lambda/2(\lambda + \mu)$.

[2] Haas, *op. cit.*, page 180.

[3] For derivation see Jeans, Dynamical Theory of Gases, Cambridge University Press (1925), Chap. XVI.

bration is

$$\bar{\epsilon} = \frac{E}{N} = \frac{h\nu}{e^{h\nu/kT} - 1} + \tfrac{1}{2}h\nu, \tag{61.3}$$

where $h\nu/2$ is the zero-point energy. The total energy is then given by

$$E = \int \bar{\epsilon} dz. \tag{61.4}$$

The limits of integration in equation (61.4) are such that the integral is taken over all modes of vibration. Since there is no limit on the frequency ν there would be an infinite number of modes and consequently an infinite energy and specific heat. However, each mode corresponds to one degree of freedom and the total number of degrees of freedom is $3N$.

The artifice used by Debye, to obviate this difficulty, was to assume that there was a maximum frequency, ν_m, such that

$$\int dz = 8\pi V \int_0^{\nu_m} \left(\frac{1}{2c_L^3} + \frac{1}{c_T^3} \right) \nu^2 d\nu = 3N, \tag{61.5}$$

or carrying out this integration,

$$\nu_m = \left(\frac{9N}{8\pi V} \right)^{1/3} \left(\frac{2c_L^3 c_T^3}{2c_L^3 + c_T^3} \right)^{1/3}. \tag{61.6}$$

Substituting from (61.2), (61.3) in (61.4),

$$E = 8\pi h V \left(\frac{1}{2c_L^3} + \frac{1}{c_T^3} \right) \int_0^{\nu_m} \left(\frac{\nu^3}{e^{h\nu/kT} - 1} + \tfrac{1}{2}\nu^3 \right) d\nu. \tag{61.7}$$

The last term of the integrand in equation (61.7) is the zero-point energy of the crystal. Substituting for $\dfrac{1}{2c_L^3} + \dfrac{1}{c_T^3}$ its value in terms of ν_m as obtained from equation (61.6), for $\nu_m = k\theta/h$ and for $\nu = xkT/h$

$$E = 9NkT \left(\frac{T}{\theta} \right)^3 \int_0^{\theta/T} \frac{x^3}{e^x - 1} dx + \tfrac{9}{8}Nk\theta. \tag{61.8}$$

The last term is the zero-point energy which is often considered as zero. The symbols defined by

$$\theta = \frac{h\nu_m}{k} \qquad \text{and} \qquad \frac{h\nu}{kT} = x \tag{61.9}$$

are used for convenience. It will be noted from equation (61.6) that

$$\theta = \frac{h}{k} \left(\frac{9N}{8\pi V} \right)^{1/3} \left(\frac{2c_L^3 c_T^3}{2c_L^3 + c_T^3} \right)^{1/3}. \tag{61.10}$$

The expression for the heat capacity at constant volume is obtained by differentiating equation (61.8) with respect to temperature

$$C_v = \left(\frac{\partial E}{\partial T} \right)_V = 9Nk \left[4 \frac{T^3}{\theta^3} I + T \left(\frac{T}{\theta} \right)^3 \frac{\partial I}{\partial T} \right], \qquad (61.11)$$

where I stands for the integral in (61.8). Now

$$\frac{\partial I}{\partial T} = \frac{\partial I}{\partial(\theta/T)} \cdot \frac{\partial(\theta/T)}{\partial T} = - \frac{\partial I}{\partial(\theta/T)} \cdot \frac{\theta}{T^2} . \qquad (61.12)$$

To evaluate $\partial I/\partial(\theta/T)$ in (61.12) it is noted that the lower limit of the integral is not a function of θ/T so that it is only necessary to differentiate the upper limit which is the indefinite integral with θ/T replacing x. The result is the integrand with θ/T replacing x; thus

$$C_v = 9Nk \left[4 \left(\frac{T}{\theta} \right)^3 \int_0^{\theta/T} \frac{x^3}{e^x - 1} dx - \left(\frac{\theta}{T} \right) \frac{1}{e^{\theta/T} - 1} \right] . \qquad (61.13)$$

Equations (61.8) and (61.13) are not very convenient for calculation but tables of $(E - E_0)/T$ and C have been computed as functions of θ/T which allow the ready application of the equations. These tables are given in Appendix IV,* Table B and Table A respectively, together with values of $(E_0 - F)/T$ (Table C).

Table XVIII illustrates the agreement between theory and experiment [1] for crystals of metallic elements. Column 1 gives the element, column 2 the density, column 3 the compressibility K, column 4 Poisson's ratio σ. With

TABLE XVIII

COMPARISON OF THE VALUES OF θ FROM SPECIFIC HEAT DATA AND DIRECT CALCULATION FROM THE ELASTIC CONSTANTS

Substance	ρ	$K \times 10^{12}$	σ	θ calc.	θ exp.
Al....	2.71	1.36	0.337	398	402
Cu....	8.96	0.74	0.334	315	332
Ag	10.53	0.92	0.379	215	214
Pb........	11.32	2.0	0.446	88	73

these elastic constants

$$c_L{}^2 = \frac{3(1 - \sigma)}{(1 + \sigma)K\rho} \quad \text{and} \quad c_T{}^2 = \frac{3(1 - 2\sigma)}{2(1 + \sigma)K\rho} . \qquad (61.14)$$

* These tables, unlike the others, are based on $R = 1.9857$; in the rare cases where accuracy warrants, the necessary corrections can be made.

[1] Born, "Atomtheorie des festen Zustandes," *Encycl. Math. Wiss.*, Vol., V, part, 3, No. 25, 27 (1923).

Column 5 gives the value of θ calculated from the elastic constants and column 6 that calculated from equation (61.13) to give the best fit with the heat capacity curves.

Figure 10 shows a graph of C_v against T/θ for certain substances. The points, as designated below the figure, represent experimental data, while the solid curve is calculated from equation (61.13). In plotting the experimental points, the value of θ used for each substance was chosen to give the best fit
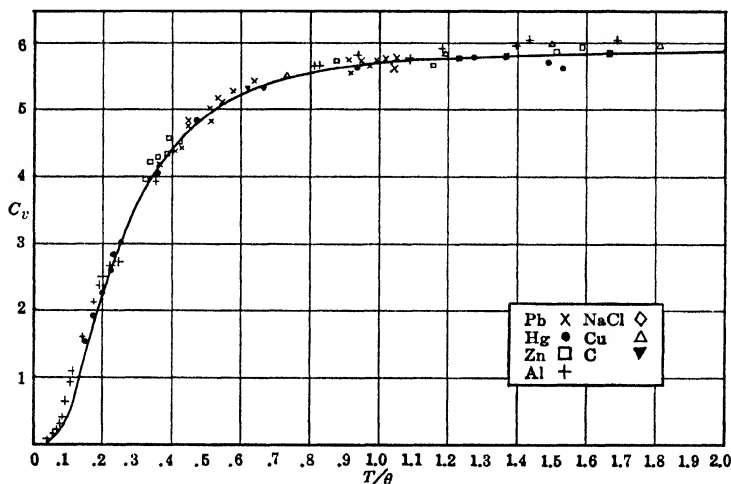
FIG. 10.   The Heat Capacity of Various Solids as Functions of T/θ

with this curve. At low temperatures θ/T is large; therefore, because of the exponential in the denominator of the second term of equation (61.13) this term is negligible. The integral in the first term becomes $\int_0^\infty x^3/(e^x - 1)dx$ because θ/T is very large on account of the smallness of T, but

$$\int_0^\infty \frac{x^3}{e^x - 1}\, dx = \frac{\pi^4}{15},$$ (61.15)

so equation (61.13) becomes

$$C_v = \frac{12\pi^4 NkT^3}{5\theta^3} = aT^3.$$ (61.16)

Similarly it can be shown that

$$E - E_0 = \frac{3\pi^4 NkT^4}{5\theta^3} = bT^4,$$ (61.17)

where E_0 is the zero-point energy. We thus see that at low temperatures the heat capacity of the postulated crystal becomes proportional to the third power of the temperature, a fact which is important in extrapolating heat capacities to $0°$ K. At high temperatures equation (61.13) becomes

$$C_v = 9Nk \left[4 \left(\frac{T}{\theta} \right)^3 \int_0^{\theta/T} x^2 dx - 1 \right], \qquad (61.18)$$

because θ/T and x are small and by expansion in series it can be shown that e^x equals $(1 + x)$; thus,

$$C_v = 9Nk[\tfrac{4}{3} - 1] = 3Nk = 3R. \qquad (61.19)$$

This result could have been predicted from the principle of equipartition. At high temperatures the crystal consists of N atoms each with three classically excited vibrational degrees of freedom. In the same way it can be shown that

$$E - E_0 = 3RT. \qquad (61.20)$$

The entropy of a perfect crystal is given by

$$S = \int_0^T C_p d \ln T = \int_0^T C_v d \ln T + \int_0^T (C_p - C_v) d \ln T, \qquad (61.21)$$

since the entropy at the absolute zero is zero. The last term of equation (61.21) is evaluated, approximately, by making use of the rule of Lindemann and Magnus [1] that

$$C_p - C_v = aT^{3/2}, \qquad (61.22)$$

whence

$$\int_0^T (C_p - C_v) d \ln T = \int_0^T aT^{1/2} dT = \tfrac{2}{3} aT^{3/2} = \tfrac{2}{3}(C_p - C_v). \qquad (61.23)$$

For a monatomic crystal the integration of the first term of (61.21) is made taking C_v as given by equation (61.13). The values of the integral (S_{Debye}) have been obtained and tabulated in Appendix IV. The tabulation is in two parts, viz.,

$$(E - E_0)/T \qquad \text{and} \qquad (E_0 - F)/T, \qquad \text{such that}$$

$$(F - E_0)/T = 3R \ln (1 - e^{-\theta/T}) - \frac{1}{3} \left(\frac{E - E_0}{T} \right), \qquad (61.24)$$

$$S = (E - E_0)/T + (E_0 - F)/T. \qquad (61.25)$$

Equation (61.24) can be obtained directly from an appropriate partition function.[2]

---

[1] *Z. Elektrochem.*, **16**, 269 (1910).

[2] See Tolman, The Principles of Statistical Mechanics, Oxford University Press (1938) page 591.

(62) **The Energy and Heat Capacity of a Crystal Composed of Molecules:**
In general each molecule has six external degrees of freedom, three of angular
oscillation or rotation and three of vibration. In the case of crystals composed
of molecules it is necessary in the above treatment to replace $3N$ by $6N$ in
equation (61.10) for calculating θ and in the equations for C_v and E (61.13)
and (61.8).[1] Thus we obtain the energy and heat capacity due to the transla-
tional and rotational degrees of freedom of the molecules which together make
up the elastic modes of vibration (Debye contributions). Suppose that the
molecules have s degrees of freedom; in general, the internal thermal motion of
the molecules will consist of $(s - 6)$ distinct modes of vibration, some of which
may have the same frequency. The energy and heat capacity due to each of
these is given by equations (43.7) and (43.8). Thus we obtain for the total
heat capacity at constant volume

$$C_v = 18R \left[4 \left(\frac{T}{\theta} \right)^3 \int_0^{\theta/T} \frac{x^3}{e^x - 1}\, dx - \left(\frac{\theta}{T} \right) \frac{1}{e^{\theta/T} - 1} \right] + \sum_{i=0}^{i=s-6} \frac{Rx_i^2 e^{x_i}}{(e^{x_i} - 1)^2}, \quad (62.1)$$

where the sum in the last term is taken over all degree of freedom and
$x_i = h\nu_i/kT$ with ν_i the frequency of the ith mode of vibration. This equation
can be written in the abbreviated form

$$C_v = C_v \text{ (acoustical)} + C_v \text{ (internal)}. \quad (62.2)$$

The thermodynamic relation required to convert the C_v to C_p for comparison
with experiment is

$$C_p - C_v = \alpha^2 V T/\beta, \quad (62.3)$$

where α is the coefficient of expansion and β the coefficient of compressibility.
It has been shown by Nernst and Lindemann[2] that an approximate form of
(62.3) is

$$C_p - C_v = 0.0214(T/T_m)C_v^2 \quad (62.4)$$

and Lord, Ahlberg and Andrews[3] have derived the relation

$$C_p - C_v = a^2 C_v^2 T, \quad (62.5)$$

where the constant a is to be determined empirically.

In Table XIX equation (62.1) has been used to calculate the heat capacity
of crystalline benzene. The value of θ was chosen as 150 to give the best agree-
ment with experiment below 50° K. The vibrational modes of benzene in cm.$^{-1}$
were taken to be:[4] $\nu_1(1) = 992.6$, $\nu_2(1) = 3061.5$, $\nu_6(2) = 608$, $\nu_7(2) = 3107$,
$\nu_8(2) = 1645$, $\nu_9(2) = 1170$, $\nu_{10}(2) = 849.7$, $\nu_{11}(1) = 783$, $\nu_{18}(2) = 1030$,

[1] Lord, Ahlberg and Andrews, *J. Chem. Phys.*, **5**, 649 (1937).

[2] *Z. Elektrochem.*, **17**, 817 (1911).

[3] *Loc. cit.*

[4] Lord and Andrews, *J. Phys. Chem.*, **41**, 149 (1937).

$\nu_{19}(2) = 1480$, $\nu_{20}(2) = 3080$, $[\nu_3(1) = 1190$, $\nu_4(1) = 538$, $\nu_5(1) = 1520$, $\nu_{12}(1) = 1008$, $\nu_{13}(1) = 3063$, $\nu_{14}(1) = 1854$, $\nu_{15}(1) = 1145$, $\nu_{16}(2) = 406$, $\nu_{17}(2) = 1160$]. The frequencies in square brackets are calculated values; the others are observed in the Raman or infra-red spectra. To obtain the value of $C_p - C_v$ the constant a in (62.5) was obtained empirically from the difference between the experimental C_p values and the calculated C_v values for temperatures above 50° K. Columns 2 and 3 respectively give the values of the first and second terms of equation (62.1) at the temperatures given in column 1. Column 4 gives the value $(C_p - C_v)$; column 5 gives the calculated C_p value (sum of columns 2, 3 and 4) while column 6 gives the experimentally observed C_p value.

TABLE XIX

HEAT CAPACITY OF BENZENE *

Temperature ° K	Acoustical C_p (Debye)	Internal C_v (Einstein)	$C_p - C_v$	Calc. C_p	Observed C_p
4	0.018			0.018	0.0195
10	.270			.270	.346
20	1.932			1.932	1.84
30	4.41		.04	4.45	4.24
40	6.45		.11	6.56	6.47
50	7.90		.20	8.10	8.14
60	8.90	0.02	.31	9.23	9.32
80	10.07	.17	.54	10.78	10.85
100	10.70	.51	.81	12.02	11.99
150	11.32	2.31	1.80	15.43	15.49
200	11.58	4.95	3.53	20.06	20.02
270	11.74	9.46	7.83	29.03	29.70

* Taken from Lord, Ahlberg and Andrews, *J. Chem. Phys.*, **5**, 649 (1937).

In the case of crystals of the alkali halides, which are really made up of ions the calculation is made on the basis of 3θ rather than 6θ (three acoustical modes for each pair of ions) and three Einstein modes are assumed for each pair of ions. For such salts the frequency of these Einstein modes of vibration can be obtained from the infra-red absorption spectrum of the crystal (Reststrahlen). In Table XX are tabulated the molal heat capacities of potassium chloride due to the elastic (Debye) modes (col. 2) and the three equal Einstein modes of vibration (col. 3). The remaining columns correspond to those of Table XIX.

At low temperatures x becomes sufficiently small for all values of ν_1 that the last term can be neglected and the heat capacity becomes

$$C_v = \frac{24\pi^4 NkT^3}{5\theta^3} = cT^3. \qquad (62.6)$$

This is the result we have anticipated earlier in connection with the experi-

TABLE XX

Heat Capacity for Mole of KCl *

T °K	Debye Term C_v	Einstein Term C	$C_p - C_v$	Calc. C_p	Observed C_p
22.8	1.04	0.046	—	1.086	1.16
26.9	1.48	0.13	—	1.61	1.52
30.1	1.87	0.25	—	2.12	1.96
33.7	2.25	0.43	—	2.68	2.50
48.3	3.52	1.43	—	4.95	5.70
57.6	4.06	2.13	0.02	6.21	6.12
70.0	4.57	2.89	0.04	7.50	7.58
86.0	4.97	3.66	0.06	8.79	8.72
235	5.81	5.55	0.32	11.68	11.78
416	5.91	5.83	0.68	12.42	12.72
550	5.93	5.87	0.90	12.70	13.10

* Taken from Nernst, "Kinetische Theorie Fester Körper," *Wolfskehl Kongress Göttingen*, **4**, 81 (1914).

mental aspects of the third law. With a T^3 law, C_v approaches zero asymptotically as T approaches zero as required.

To obtain the entropy of a crystal composed of molecules it is merely necessary to obtain the entropy due to the lattice modes from the tables of Appendix IV as outlined at the end of the previous paragraph but using a value of θ compatible with (62.1) (i.e., based on $6N$) and to add the entropy due to the internal modes of vibration of the molecules.

MAGNETIC COOLING

(63) **Paramagnetism**: The theory to be developed applies strictly to gases only, but it may also be applied to solutions of the paramagnetic substance and to solids in which the magnetic particles are widely separated.

Any substance with an appreciable number of elementary particles (atoms, ions or molecules) with a non-zero value of the inner quantum number J * will be paramagnetic. This paramagnetism is the result of a diamagnetic effect and a paramagnetic effect. The diamagnetic effect is due to the second order interaction of the orbital motion of the electrons with the field. The paramagnetic effect is present whenever J is not zero and is due to a magnetic moment which is the resultant of the "equivalent magnetic shells" associated with the electronic orbits or spins or with both. In general the diamagnetic effect of each atom is small compared to the paramagnetic effect. Diamagnetic effects can make an appreciable negative contribution to the susceptibility when there are a number of diluting atoms or groups without magnetic moments. The susceptibility can be corrected for this effect by adding the nu-

* In the following discussion J always refers to the vector sum of L and S. It is not to be confused with J used for the rotational quantum number in earlier paragraphs.

merical value of the diamagnetic susceptibility of a similar system but without the paramagnetic effects. Thus a susceptibility, due only to the magnetic moments of the particles, is obtained. It will be assumed that all experimental susceptibilities have been corrected in this manner.

Let $\epsilon_{J, M}$ denote the energy of a particle in a magnetic field of strength H; the subscripts denote that this value of the energy is not only affected by the inner quantum number J, but also by the usual magnetic quantum number M which expresses the orientation of the resultant electronic angular momentum with respect to the field; M can have all the values J, $J - 1$, $\cdots$, 0, $\cdots$, $-(J - 1)$, $-J$. The component of the magnetic moment of the particle parallel to the field, H, is related to the energy in the field by

$$\mu_{J, M} = -\partial\epsilon_{J, M}/\partial H. \qquad (63.1)$$

The total magnetization per mole of substance (magnetic moment per gram mole of substance) is obtained by summing the individual contributions of the quantum states

$$I_m = \frac{N \sum_{J, M} \mu_{J, M} e^{-\epsilon_{J, M}/kT}}{\sum_{J, M} e^{-\epsilon_{J, M}/kT}} \cdot \qquad (63.2)$$

The denominator of this expression is the partition function Q; thus we obtain

$$I_m = NkT\partial \ln Q/\partial H \qquad (63.3)$$

as can be seen by direct differentiation and substitution of (63.1).

The total magnetic moment of a particle is

$$\mu = g\beta \sqrt{J(J + 1)}, \qquad (63.4)$$

where g is the Landé splitting factor given by

$$g = 1 + \frac{J(J + 1) + S(S + 1) - L(L + 1)}{2J(J + 1)} \qquad (63.5)$$

and β is the Bohr magneton defined by

$$\beta = \frac{|e|h}{4\pi m_e c} = 0.917 \times 10^{-20} \text{ ergs/gauss.}$$

The component of the magnetic moment parallel to a field of strength H is

$$\mu_H = Mg\beta + bH, \qquad (63.6)$$

where the term bH is a result of the perturbation by the field. Thus, by

reference to (63.1), the energy in a field of strength H is seen to be

$$\epsilon_{J,M} = \epsilon_J{}^0 - Mg\beta H - \tfrac{1}{2}bH^2, \tag{63.7}$$

where $\epsilon_J{}^0$ is the energy in the absence of the field which is of course independent of M.

(64) **The Langevin-Debye Theory of Paramagnetism:** [1] Consider a particle with its lowest state having a non-zero value of J. In general, states with higher values of J result by changing the orientation of the vector J with respect to the vector S. As a rule these states will be of sufficiently higher energy than the ground state that the number of particles in them is negligible. The energy of any particle in a field is given by (63.7) and the moment by (63.6); the value of b is sufficiently small that the terms involving it can be neglected. The total magnetization per mole is then obtained by means of (63.2); since there is only one state in the absence of the field (one value of J) the summation of J may be omitted and the equation becomes

$$I_m = \frac{Ne^{-\epsilon_J{}^0/kT} \sum\limits_{M=-J}^{M=+J} g M \beta e^{g M \beta H/kT}}{e^{-\epsilon_J{}^0/kT} \sum\limits_{M=-J}^{M=+J} e^{g M \beta H/kT}}. \tag{64.1}$$

Because the exponents are small compared to unity, the exponentials can be replaced by the first two terms of their power expansion; thus,

$$I_m = \frac{N \sum\limits_{M=-J}^{M=+J} g M \beta [1 + g M \beta H/kT]}{\sum\limits_{M=-J}^{M=+J} (1 + g M \beta H/kT)}. \tag{64.2}$$

Since

$$\sum_{M=-J}^{M=+J} g\beta M = 0,$$

while, in the denominator, the terms $gM\beta H/kT$ cancel, and unity appears $(2J + 1)$ times,

$$I_m = \frac{Ng^2\beta^2 H}{kT} \cdot \frac{\sum\limits_{-J}^{+J} M^2}{2J + 1} = \frac{J(J + 1)Ng^2\beta^2 H}{3kT}. \tag{64.3}$$

---

[1] For an excellent discussion of the subject of paramagnetism see Van Vleck, Theory of Electric and Magnetic Susceptibilities, Oxford (1932).

The total magnetic susceptibility per mole is then

$$\chi_m = \frac{I_m}{\mathrm{II}} = \frac{J(J+1)Ng^2\beta^2}{3kT} = \frac{\mu^2 N}{3kT}. \tag{64.4}$$

We have thus obtained a theoretical justification of Curie's Law

$$\chi_m = C_1/T, \tag{64.5}$$

where C_1 is called the Curie constant, which is given by

$$C_1 = \frac{J(J+1)Ng^2\beta^2}{3k} = \frac{\mu^2 N}{3k}. \tag{64.6}$$

Introducing a new quantity, the magnetic moment per mole

$$\mu_m = \mu N = Ng\beta\sqrt{J(J+1)}, \tag{64.7}$$

$$C_1 = \mu_m{}^2/3R, \tag{64.8}$$

$$\chi_m = \mu_m{}^2/3RT. \tag{64.9}$$

Theoretical values of μ_m can be calculated from (64.7). Experimental values can be obtained from the measured susceptibility and equation (64.9) or by finding the Curie constant from the temperature coefficient of susceptibility and then using equation (64.8); then

$$\mu_m = (3RT\chi_m)^{1/2} = (3RC_1)^{1/2}.$$

Table XXI compares the theoretical and measured values of μ_m for a number of rare earth ions in terms of the molal Bohr magneton (B) as the unit, where $B = N\beta = 5589$ e.m.u. per mole. The measured quantity

$$\left(\frac{3RT\chi_m}{B^2}\right)^{1/2} = \frac{\sqrt{3RC_1}}{B} = \mu_{\mathrm{eff.}} \tag{64.10}$$

is called the "effective Bohr magneton number"; its theoretical value is μ/β. It is to be noted that if Curie's law is not obeyed (i.e., if C_1 is dependent on temperature) $\mu_{\mathrm{eff.}}$ is temperature dependent. The theoretical values in the eighth column are those calculated by Hund using (63.4). Those in the ninth column will be discussed presently. The observed values in column ten were obtained from values on solution and on the solid state; they agree with the theoretical values of Hund [1] except in the case of Sm^{+++} and Eu^{+++}. The reason for this has been attributed to the incorrectness of the assumption that the levels with higher J values are present in inappreciable quantities; i.e.,

[1] *Z. Physik*, **33**, 85 (1925).

TABLE XXI

CALCULATED AND OBSERVED EFFECTIVE BOHR MAGNETON NUMBERS FOR THE IONS
OF THE RARE EARTH METALS *

Ion	No. of $4f$ Electrons	Normal State	S	L	J	g	Effective Magneton Numbers		
							Calc. Hund	Calc. Van Vleck	Obs.†
La^{+++}	0	$^1S_0$	0	0	0	—	0	0.00	0
Ce^{+++}	1	$^2F_{5/2}$	$\frac{1}{2}$	3	$\frac{5}{2}$	$6\frac{2}{7}$	2.54	2.56	2.4
Pr^{+++}	2	$^3H_4$	1	5	4	$4\frac{4}{5}$	3.58	3.62	3.5
Nd^{+++}	3	$^4I_{9/2}$	$\frac{3}{2}$	6	$\frac{9}{2}$	$8\frac{8}{11}$	3.62	3.68	3.5
Il^{+++}	4	$^5I_4$	2	6	4	$3\frac{3}{5}$	2.68	2.83	—
Sm^{+++}	5	$^6H_{5/2}$	$\frac{5}{2}$	5	$\frac{5}{2}$	$2\frac{2}{7}$	0.84	1.55, 1.65	1.5
Eu^{+++}	6	$^7F_0$	3	3	0	—	0	7.94	3.6
Gd^{+++}	7	$^8S_{7/2}$	$\frac{7}{2}$	0	$\frac{7}{2}$	2	7.94	7.94	8.0
Tb^{+++}	8	$^7F_6$	3	3	6	$3\frac{1}{6}$	9.72	9.7	9.5
Ds^{+++}	9	$^6H_{15/2}$	$\frac{5}{2}$	5	$15\frac{1}{2}$	$4\frac{4}{3}$	10.65	10.6	10.7
Ho^{+++}	10	$^5I_8$	2	6	8	$5\frac{5}{4}$	10.61	10.6	10.3
Er^{+++}	11	$^4I_{15/2}$	$\frac{3}{2}$	6	$15\frac{1}{2}$	$6\frac{6}{5}$	9.58	9.6	9.5
Tu^{+++}	12	$^3H_6$	1	5	6	$7\frac{7}{6}$	7.56	7.6	7.3
Yb^{+++}	13	$^2F_{7/2}$	$\frac{1}{2}$	3	$\frac{7}{2}$	$8\frac{8}{7}$	4.54	4.5	4.5
Lu^{+++}	14	$^1S_0$	0	0	0	—	0	0.00	0

* Taken from Fowler and Guggenheim, Statistical Thermodynamics, Cambridge University Press, 1939, page 622.

† These values are averages given by Stoner, Magnetism and Matter, Methuen (1934), of various experimental values, some on solid hydrated sulfates, others on aqueous solutions of sulfates or nitrates. For more detailed values, see Van Vleck, op. cit., p. 243.

that $\epsilon^0{}_{J+1} - \epsilon^0{}_J \gg kT$. If this condition is not fulfilled equation (63.2) must be used in the calculation and terms in b can no longer be neglected. Such values have been calculated by Van Vleck and Frank[1] and are given in column nine.

(65) **Quenching of Orbital Angular Momentum:** It can be shown that, in the case of the transition elements, the orbital angular momentum (as represented by L) is quenched by interaction with the field of the surrounding ions. The orbital angular momentum can no longer be oriented by the field. The spin moment, however, is unaffected; thus, $L = 0$, $J = S$, $g = 2$ so that in place of (63.4) we use $\mu_e = g\beta\sqrt{S(S+1)}$,

$$\therefore \quad I_m = \frac{4S(S+1)N\beta^2 H}{3kT}. \tag{65.1}$$

The Curie constant is given by

$$C_1 = \frac{4S(S+1)N\beta^2}{3k}, \tag{65.2}$$

[1] Van Vleck and Frank, *Phys. Rev.*, **34**, 1494, 1625 (1929); Frank, *ibid.*, **39**, 119 (1932).

and

$$\mu_{\text{eff.}} = \left(\frac{3RT\chi_m}{B^2}\right)^{1/2} = \frac{\sqrt{3RC_1}}{B} = 2\sqrt{S(S+1)}. \tag{65.3}$$

Table XXII compares the theoretical and measured value of μ_m/β for the ions of a number of transition elements. Columns eight and nine were calculated by the methods used for the rare earth ions by Hund and Van Vleck respectively.

TABLE XXII

CALCULATED AND OBSERVED EFFECTIVE BOHR MAGNETON NUMBERS OF IONS OF THE TRANSITION ELEMENTS OF THE IRON GROUP *

Ion	No. of $3d$ Electrons	Normal State	S	L	J	g	Effective Magneton Numbers			
							Calc. Hund	Calc. Van Vleck	Calc. Stoner	Obs.†
K^+, V^{5+} ..	0	$^1S_0$	0	0	0	—	0.00	0.00	0.00	0.00
Sc^{++} Ti^{+++} V^{++++}	1	$^2D_{3/2}$	$1\frac{1}{2}$	2	$3\frac{1}{2}$	$4\frac{4}{5}$	1.55	2.57/2.18/1.78	1.73	1.75
Ti^{++} V^{+++}	2	$^3F_2$	1	3	2	$2\frac{2}{3}$	1.63	3.36/2.73	2.83	2.76–2.85
V^{++} Cr^{+++} Mn^{++++}	3	$^4F_{3/2}$	$3\frac{1}{2}$	3	$3\frac{1}{2}$	$2\frac{2}{5}$	0.77	3.60/2.97/2.47	3.87	3.81–3.86/3.68–3.86/4.00
Cr^{++} Mn^{+++}	4	$^5D_0$	2	2	2	0	0.00	4.25/3.80	4.90	4.80
Mn^{++} Fe^{+++}	5	$^6S_{5/2}$	$5\frac{1}{2}$	0	$5\frac{1}{2}$	2	5.92	5.92/5.92	5.92	5.2–5.96/5.94
Fe^{++}......	6	$^5D_4$	2	2	4	$3\frac{1}{2}$	6.70	6.54	4.90	5.33
Co^{++}......	7	$^4F_{9/2}$	$3\frac{1}{2}$	3	$9\frac{1}{2}$	$4\frac{4}{3}$	6.64	6.56	3.87	4.6–5.0
Ni^{++}.......	8	$^3F_4$	1	3	4	$5\frac{1}{4}$	5.59	5.56	2.83	3.23
Cu^{++}......	9	$^2D_{5/2}$	$1\frac{1}{2}$	2	$5\frac{1}{2}$	$6\frac{6}{5}$	3.55	3.53	1.73	1.8–2.0
Cu^+, Zn^{++}.	10	$^1S_0$	0	0	0	—	0.00	0.00	0.00	0.00

* Taken from Fowler and Guggenheim, Statistical Thermodynamics, Cambridge University Press, 1939, page 625.

† The experimental values are from Van Vleck, *op. cit.*, p. 285; they are for aqueous solutions. Values for the solid salts do not differ greatly from those for solutions.

The results in column ten were calculated by Stoner using equation (65.3).[1] The experimental values in column 11 show that the last is the correct procedure.

(66) **Magnetic Saturation at Low Temperatures:** In the application of equation (64.1) it was tacitly assumed that $\beta H/kT \ll 1$. At low temperatures or high field strengths or both, this may not be the case and, in general, it is not possible to expand the exponentials as a power series. The partition function for a ^{2S+1}S state is

$$Q = \sum_{M=-S}^{M=+S} e^{2M\beta H/kT} = \frac{\sinh\{(2S+1)\beta H/kT\}}{\sinh\{\beta H/kT\}} \qquad (66.1)$$

and then

$$I_m = NkT\partial \ln Q/\partial H \qquad (66.2)$$

$$= \beta N \left[(2S+1) \coth \left\{ \frac{(2S+1)\beta H}{kT} \right\} - \coth\{\beta H/kT\} \right]. \qquad (66.3)$$

For large values of $\beta H/kT$ this becomes

$$I_m = 2N\beta S, \qquad (66.4)$$

which corresponds to saturation, with each magnetic particle lined up with the field. The considerations of this paragraph also apply to ions of the transition elements such as Cr^{+++} which are effectively in S states due to the "freezing in" of the orbital angular momentum.

(67) **Entropy of Ideal Paramagnetic Salts:** It is convenient to consider the entropy of a paramagnetic salt at low temperatures as made up of a contribution due to the orientation of the electronic angular momentum (J) and a contribution due to all the other degrees of freedom. Nuclear spin is not considered. Apart from the orientations of J, the degrees of freedom of lowest energy are the acoustical (Debye) modes of vibration of the lattice and, since even the contribution of these is small, all others can be neglected.

Only paramagnetic ions in S states $(J = S)$ such as Gd^{+++}, or those that are effectively in S states, as is the case for the transition elements, will be considered. Denoting the entropy due to the orientation of the spins (spin system) by S^{Sp} and that due to the lattice by S^{Ac}, then

$$S = S^{Sp} + S^{Ac}. \qquad (67.1)$$

Assuming ideal conditions the partition function for the spins in a magnetic field H is

$$Q(H, T) = \frac{\sinh\{(2S+1)\beta H/kT\}}{\sinh\{\beta H/kT\}}, \qquad (67.2)$$

$$S^{Sp} = R \left[\frac{T}{Q(H, T)} \cdot \frac{\partial Q(H, T)}{\partial T} + \ln Q(H, T) \right]. \qquad (67.3)$$

[1] Stoner, *Phil. Mag.*, **8**, 250 (1929).

From (67.2) and (67.3) it follows that

$$S^{Sp} = R\left[\ln\frac{\sinh\{(2S+1)x\}}{\sinh x}\right.$$

$$\left. - (2S+1)x\coth\{(2S+1)x\} + x\coth x\right], \quad (67.4)$$

where $x = \beta\mathrm{II}/kT$. If H is small, i.e., x is small, (67.4) becomes

$$S^{Sp} = R\left[\ln(2S+1) - \tfrac{1}{6}\frac{4S(S+1)\beta^2\mathrm{H}^2}{k^2T^2}\right], \quad (67.5)$$

and in the absence of a magnetic field

$$S^{Sp} = R\ln(2S+1). \quad (67.6)$$

This is the expected result since there are $2S+1$ positions of the spin of equal energy. The entropy of mixing of these is just (67.6). It is to be noted that (67.6) shows the heat capacity of the spin system in the absence of a field to be zero, and predicts an entropy of $R\ln(2S+1)$ at the absolute zero. In the next section we shall see what causes the removal of this entropy in any real case.

(68) **Heat Capacity and Entropy of Paramagnetic Salts with Crystalline Stark Effect:** It should be noted that (67.2) is true only when the external magnetic field effect is large compared with the crystalline Stark effect and the interaction between spins. This is generally the case, but at zero field and low temperatures the crystalline Stark effect and the interaction between spins become appreciable, and equation (67.6) is no longer true. We shall discuss only the crystalline Stark effect in detail.

The energies of the $2S+1$ spin orientations of an ^8S state (e.g., Gd^{+++}) have been deduced by Van Vleck and Penney.[1] They assumed an electric field of cubic symmetry and deduced that the eight degenerate levels of the field-free ion are split into three levels of different energy, viz., two doubly degenerate and one quadruply degenerate, the latter having an energy lying between the energies of the two former. The appropriate partition function is then

$$Q = 2 + 4e^{-3\delta/8kT} + 2e^{-\delta/kT} \quad (68.1)$$

or

$$Q = 2 + 4e^{-5\delta/8kT} + 2e^{-\delta/kT}, \quad (68.2)$$

corresponding to energies 0, $\tfrac{3}{8}\delta$, and δ, or 0, $\tfrac{5}{8}\delta$ and δ, where δ is the total separation. There is no theoretical means of deciding between the alternatives.

[1] *Phil. Mag.*, **17**, 961 (1934).

Hebb and Purcell[1] favor the partition function (68.1), because it agrees better with experiment, and from it have derived the entropy in the customary manner, namely

$$S^{Sp} = R \left[\frac{\delta}{2kTQ} (3e^{-3\delta/8kT} + 4e^{-\delta/kT}) + \ln Q \right]. \tag{68.3}$$

The value of δ is taken to give the best fit with the experimental data which are obtained by a method which will be discussed presently. The important thing to notice is that, at the absolute zero, the entropy remaining is $R \ln 2$ instead of $R \ln 8$. There is no doubt however that the interaction between spins, neglected in the treatment just outlined, will remove even this entropy in a manner analogous to that by which the crystalline Stark effect removes $R \ln 4$ units.

The heat capacity as a result of the crystalline Stark effect can be obtained through its usual connection with the partition function.

To obtain the total entropy the lattice entropy (S^{Ac}) must be added to S^{Sp}. The lattice entropy is given by

$$S^{Ac} = \frac{\text{const.}}{3} T^3 \tag{68.4}$$

at the temperatures under discussion; below $4°$ K this is negligible.

The lattice heat capacity is given by

$$C^{Ac} = \text{const.} \times T^3 = 3S^{Ac}. \tag{68.5}$$

(69) **Thermodynamic Relations in a Magnetic Field:** It has already been noted that the intensity of magnetization induced by a magnetic field bears a relation to the partition function as is also the case for the entropy. A relation between the latter and the intensity of magnetization can be derived by purely thermodynamic reasoning which is quite independent of any theory of paramagnetism.[2]

Whenever the intensity of magnetization of matter changes reversibly as the result of the application of a magnetic field the work, $- \delta W$, done * *by the field*, H, is

$$- \delta W = dA = HdI, \tag{69.1}$$

where I is the intensity of magnetization. Applying the first and second laws to a reversible system at constant temperature where the only forces acting

---

[1] *J. Chem. Phys.*, **5**, 338 (1937).

[2] See Giauque, *J. Am. Chem. Soc.*, **49**, 1864 (1927).

* It is to be noted that by definition the work (δW) is *positive* when work is done *by the substance on the field.*

are an external pressure and an external magnetic field

$$dE = TdS - PdV + \mathrm{H}dI. \tag{69.2}$$

In view of this equation it is convenient and consistent to define the heat content (enthalpy) as

$$H = E + PV - \mathrm{H}I \tag{69.3}$$

and

$$F = H - TS = E + PV - \mathrm{H}I - TS. \tag{69.4}$$

Using (69.3), equation (69.2) becomes

$$TdS = dH + Id\mathrm{H} - \dot{V}dP. \tag{69.5}$$

For the special case of constant pressure and magnetic field

$$TdS = dH, \tag{69.6}$$

so that,

$$(\partial H/\partial S)_{P,\mathrm{H}} = T \tag{69.7}$$

or

$$(\partial S/\partial T)_{P,\mathrm{H}} = (1/T)(\partial H/\partial T)_{P,\mathrm{H}} = C_{P,\mathrm{H}}/T, \tag{69.8}$$

where $C_{P,\mathrm{H}}$ is the heat capacity at constant pressure and constant field. Since equation (69.5) applies at constant temperature, by considering a process in which the field is changed at constant pressure

$$T(\partial S/\partial \mathrm{H})_{T,P} = (\partial H/\partial \mathrm{H})_{T,P} + I. \tag{69.9}$$

Differentiating with respect to temperature at constant pressure and magnetic field

$$(\partial S/\partial \mathrm{H})_{T,P} + T(\partial^2 S/\partial \mathrm{H}\partial T)_P = (\partial^2 H/\partial \mathrm{H}\partial T)_P + (\partial I/\partial T)_{P,\mathrm{H}}.$$

In view of equation (69.8) the last term on the left and the first on the right are equal so

$$(\partial S/\partial \mathrm{H})_{T,P} = (\partial I/\partial T)_{P,\mathrm{H}} \tag{69.10}$$

or

$$(\partial S/\partial \mathrm{H})_{T,P} = \mathrm{H}(\partial \chi/\partial T)_{P,\mathrm{H}}. \tag{69.11}$$

Integrating (69.11) between two values of the field

$$S_2 - S_1 = \int_{\mathrm{H}_1}^{\mathrm{H}_2} \mathrm{H}(\partial \chi/\partial T)_{P,\mathrm{H}}d\mathrm{H}. \tag{69.12}$$

If Curie's law is obeyed

$$S_2 - S_1 = - \text{const.} \int_{H_1}^{H_2} (H/T^2)dH = \frac{\text{const.}}{2T^2} (H_1{}^2 - H_2{}^2). \quad (69.13)$$

Finally it is evident that

$$(\partial F/\partial H)_{P,T} = - I \quad (69.14)$$

and

$$(\partial F/\partial T)_{H,P} = - S. \quad (69.15)$$

It will be shown later how equation (69.7) is used to determine the thermodynamic temperature scale at low temperatures.

(70) **Cooling by Adiabatic Demagnetization**: The principles underlying magnetic cooling were first enunciated by Giauque [1] and independently by Debye.[2] When a paramagnetic substance in an S state or an effective S state is magnetized at low temperatures, equation (67.4) shows that the spin entropy decreases below the field-free value. The heat evolved may be conducted away to a bath of liquid helium evaporating under reduced pressure and finally the substance thermally isolated. The reduction of the field then constitutes a reversible isentropic process. When the field is reduced the entropy must stay constant; consequently the temperature must fall.

Ordinarily the entire entropy is due to the spins. Thus during the demagnetization

$$S^{Sp} = \text{constant.} \quad (70.1)$$

The application of equation (67.4) to Gd^{+++} (^8S state) shows that, by applying a field of 20,000 gauss and at a temperature of $4°$ K, the entropy per gram-ion is reduced from $2.09 R$ to $1.40 R$. After removal of heat and thermal isolation, if the field is reduced to 8000 gauss equation (67.4) shows that T must fall to $1.6°$ K in order to keep S^{Sp} constant. Since equation (67.4) shows that S^{Sp} is a function only of H/T it is seen that for the adiabatic demagnetization of any ideal paramagnetic substance in an S state with negligible lattice entropy

$$H/T = \text{constant.} \quad (70.2)$$

Thus, in a perfectly general way, the temperatures during adiabatic demagnetization of any ideal paramagnetic substance in an S state are proportional to the field strength.

If equation (67.4) were applicable at the very lowest temperature, reduction of the field to zero would result in attainment of the absolute zero. However, long before this temperature is reached the effect of splitting of the $2S + 1$ levels becomes appreciable. Returning to the previous example, the spin entropy of Gd^{+++}, at low temperatures with zero field, is determined by (68.3). If δ could be calculated theoretically this equation could be used to calculate

---

[1] Address by W. M. Latimer, California Section American Chemical Society, April 9, 1926; Giauque, *J. Am. Chem. Soc.*, **49**, 1864, 1870 (1927),

[2] *Ann. Physik*, **81**, 1154 (1926).

the temperature reached at zero field. In practice, however, the measured temperatures attained in such experiments on reduction of the field to zero allow the value of δ to be determined. In other words the entropy before demagnetization (in the example cited, 1.40 R per mole) is the value of the entropy for zero field at the final temperature attained after adiabatic demagnetization. Thus it is possible to construct an experimental curve of entropy versus temperature in the absence of a magnetic field. It should be noted that the effect of splitting is usually negligible in the presence of the field; it is for this reason that equation (67.4) can be used. If the effect of splitting is not negligible, a correction must be applied.
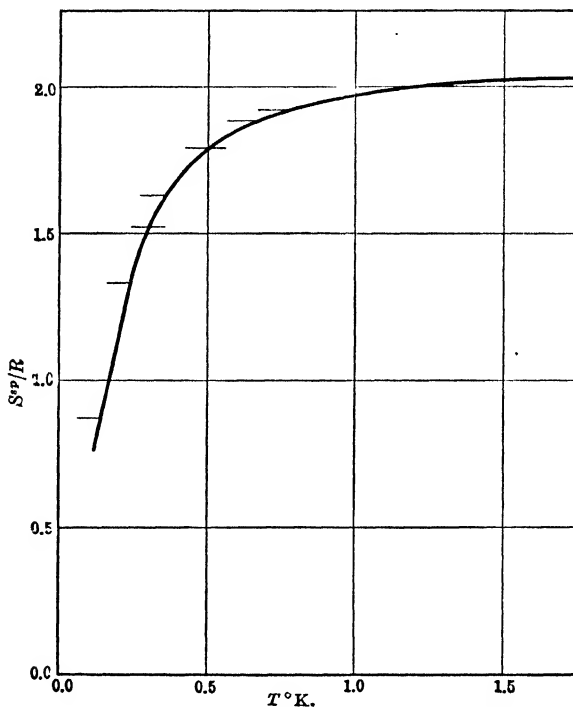
FIG. 11.   The Molecular Entropy for Zero Field
of $Gd(O_3SC_6H_4NO_2)_3 \cdot 7H_2O$

Hebb and Purcell chose a value of δ/k of 1.4° K to obtain the best fit with the experimental zero field entropies for gadolinium nitrobenzene sulfonate heptahydrate as determined by MacDougall and Giauque.[1] The values of S/R for zero field calculated by Hebb and Purcell are given in Fig. 11. The

[1] *J. Am. Chem. Soc.*, **58**, 1032 (1936).

horizontal bars represent the experimental entropies of MacDougall and Giauque; the length of each bar indicates the uncertainty in the temperature scale. The curve shows that starting with gadolinium nitrobenzene sulfonate at 4° K and a field of 20,000 gauss (entropy of 1.40 R per gram ion), adiabatic demagnetization to zero field produces a temperature of 0.27° K.

At the low temperatures attained it is not possible to use helium gas thermometers or helium vapor pressure thermometers. The most convenient method to measure the temperature is to make use of the magnetic susceptibility of the paramagnetic substance used in cooling. If the substance obeys Curie's law,

$$T = C_1/\chi_m, \qquad (70.3)$$

the absolute temperature is inversely proportional to the susceptibility. The proportionality constant can be obtained by determining the susceptibility at the temperature of the liquid helium bath as indicated by its vapor pressure. Usually the substance does not exactly follow Curie's law so that the temperatures calculated from (70.3) and denoted by T^* are not true Kelvin temperatures. The manner in which values of T^* are related to T will be discussed below.

To measure the susceptibility, the sample tube is surrounded with a closely fitting solenoid

FIG. 12. Apparatus for Attainment of Low Temperatures by Adiabatic Demagnetization

which is coaxial with it. The inductance of this solenoid measures the magnetic permeability from which the susceptibility can be calculated.

A schematic diagram of the apparatus used in adiabatic demagnetization experiments is shown in Fig. 12, labelled in such a way that its operation is self explanatory.

Figure 13 is a graph of the entropy of iron ammonium alum plotted against temperature. The solid curve is for zero field, whereas the circles represent the entropy at the indicated value of the field. To find the temperature reached on reduction to zero field starting at a given temperature and field strength, it is merely necessary to draw a line parallel to the temperature axis

through the point corresponding to the initial conditions. The temperature
where this line intersects the curve of zero field is the temperature reached
when the field is reduced to zero.
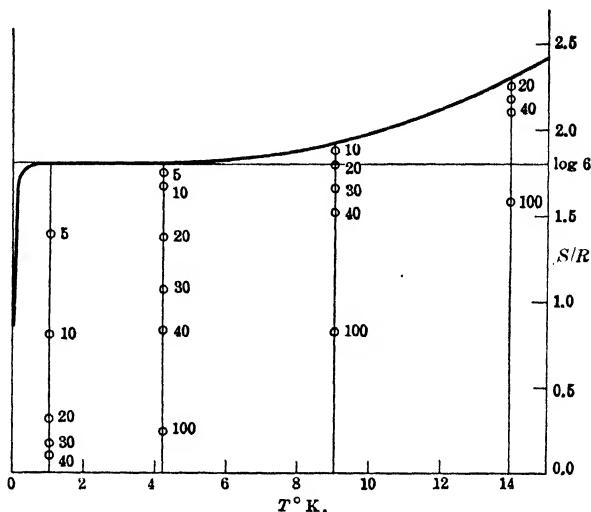
Fig. 13. Molecular Entropy of $NH_4Fe(SO_4)_2 \cdot 12H_2O$. Magnetic field strength in kilogauss
are represented by numbers scattered over the diagram

For any paramagnetic substance

$$dS = (\partial S/\partial T)_{P,H}\, dT + (\partial S/\partial H)_{P,T}\, dH. \tag{70.4}$$

For an isentropic process $dS = 0$; thus

$$(\partial T/\partial H)_{P,S} = -(\partial S/\partial H)_{P,T}/(\partial S/\partial T)_{P,H} = -(TH/C_{P,H})(\partial \chi/\partial T)_{P,H}, \tag{70.5}$$

after using (69.8) and (69.11). This relation for the temperature change on
adiabatic demagnetization is independent of any theory of paramagnetism.

Table XXIII shows the temperatures attained in experiments, the first of

TABLE XXIII

TEMPERATURES OBTAINED BY ADIABATIC DEMAGNETIZATION OF $Gd_2(SO_4)_3 \cdot 8H_2O$
FROM 1.36° K AND FIELD H

H, gauss......	4575	6200	6860	7920	7920	7920
T, ° K......	0.492	0.346	0.315	0.258	0.260	0.258

their kind, in which the magnetic field surrounding a sample of gadolinium
sulfate octahydrate initially at 1.36° K was reduced adiabatically to zero.[1]

[1] Giauque and MacDougall, *Phys. Rev.*, **43**, 768 (1933); *J. Am. Chem. Soc.*, **57**, 1175 (1935.)

TABLE XXIV

TEMPERATURES ATTAINED BY ADIABATIC DEMAGNETIZATION OF VARIOUS
PARAMAGNETIC SALTS *

Experimenters	Date	Salt	Initial Field (Gauss)	Initial Temp. (° K)	Final Temp. (° Curie)
Giauque and MacDougall [a].	1933	Gadolinium sulfate	8000	1.5	0.25
de Haas, Wiersma and Kramers [b]..	1933	Cerium fluoride Dysprosium ethyl-sulfate Cerium ethyl-sulfate	27600 19500 27600	1.35 1.35 1.35	0.13 0.12 0.085
de Haas and Wiersma [c]....	1934	Chromium-potassium alum	24600	1.16	0.031
de Haas and Wiersma [d].....	1935	Iron-ammonium alum 1 chromium-potassium alum + 14.4 aluminum-potassium alum	24075 24075	1.20 1.29	0.018 0.0044
de Haas and Wiersma [e].... .	1935	Cesium-titanium alum	24075	1.314	0.0055
Kürti and Simon [f]...	1935	Gadolinium sulfate Manganese-ammonium sulfate Iron-ammonium alum 1 manganese-ammonium sulfate + 20 magnesium-ammonium sulfate	5400 8000 14100 8300 4950 —	1.15 1.23 1.23 1.23 1.23 —	0.35 0.09 0.038 0.072 0.114 0.05
MacDougall and Giauque [g] .	1936	Gadolinium nitrobenzene-sulfonate	8090	0.94	0.098
Kürti, Lainé, Rollin and Simon [h]........... . .	1936	Iron-ammonium alum	32000	1.08	0.010
Kürti, Lainé and Simon [i]....	1939	Iron-ammonium alum	28800	8.5	0.36
Ashmead [j].....	1939	Copper-potasium sulfate	35900	1.17	0.005

* Taken from Burton, Grayson Smith, and Wilhelm, Phenomena at the Temperature of Liquid Helium, p. 227, Reinhold Publishing Corp., New York, 1940.

[a] Giauque and MacDougall, *Phys. Rev.*, **43**, 768 (1933).

[b] de Haas, Casimir and Kramers, *Physica*, **13**, 175 (1933); *ibid.* (new series), **1**, 1 (1933).

[c] de Haas and Wiersma, *ibid.*, **1**, 779 (1934).

[d] *Idem, ibid.*, **2**, 335 (1935).

[e] *Idem, ibid.*, **2**, 438 (1935).

[f] Kürti and Simon, *Proc. Roy. Soc.*, **A**, **149**, 152 (1935).

[g] MacDougall and Giauque, *J. Am. Chem. Soc.*, **58**, 1032 (1936).

[h] Kürti, Lainé, Rollin and Simon, *Compt. rend.*, **202**, 1576 (1936).

[i] Kürti, Lainé and Simon, *ibid.*, **208**, 173 (1939).

[j] Ashmead, *Nature*, **143**, 853 (1939).

Table XXIV gives the lowest values of the temperature attained in other investigations of this kind.

(71) **The Thermodynamic Temperature Scale below 1° K:** It has already been pointed out that the Curie law does not hold strictly at these temperatures. True thermodynamic temperatures can be obtained by using (69.7): this equation can be rewritten

$$T = (\partial H/\partial T^*)_{PH}/(\partial S/\partial T^*)_{PH} \tag{71.1}$$

or since the PV effects are small

$$T = (\partial E/\partial T^*)_H/(\partial S/\partial T^*)_H, \tag{71.2}$$

where the partial differentiation is with respect to Curie temperatures. For the case of zero field the denominator can be obtained from the experimental
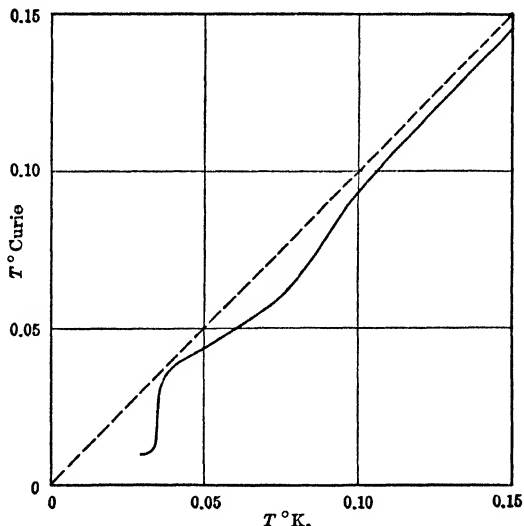
Fig. 14.   Comparison of Curie Temperature Scale for Iron-Ammonium Alum
with the Thermodynamic Scale

curve of entropy plotted against Curie temperature for zero field. The data are obtained by observing the final Curie temperatures produced by reducing the magnetic field adiabatically to zero with various starting conditions for which the entropy is calculated using (67.4). The numerator is simply the heat capacity at constant field (in this case zero); it can be found by measuring the small rise in the Curie temperature for various additions of energy. Giauque and MacDougall [1] use an induction heater for the introduction of energy,

---

[1] *Phys. Rev.*, **47**, 885 (1935); *J. Am. Chem. Soc.*, **60**, 376 (1938).

whereas Kürti, Lainé and Simon [1] use γ rays of known intensity for this purpose. In Fig. 14 the Curie temperature scale (ordinate) for iron ammonium alum is compared with the thermodynamic scale (abscissa). The solid curve gives the experimental results and the dotted line shows the behavior to be expected if the Curie law were strictly true for this substance.

(72) **The Entropy of Crystals at the Absolute Zero:** At the absolute zero a perfect crystal consists of a definitely ordered state of matter represented by a single wave function such as

$$\psi_1 = \phi_1(1)\phi_2(2) \cdots \phi_N(N), \tag{72.1}$$

where the wave functions ϕ_1, ϕ_2, etc. can be regarded as the eigenfunctions of lowest energy for the single particles. The wave functions ϕ_1 are such that they correspond to a probability $(\phi_1\phi_1^*)$ of almost unity of finding the particle in a very narrow region in space, and zero probability of finding it elsewhere. This situation is entirely compatible with the principle of uncertainty which says that the product of the uncertainty in the position, δq, and the uncertainty in the momentum, δp, is given by

$$\delta q \delta p = h, \tag{72.2}$$

because the particles are not at rest but have a momentum associated with their zero-point energy.

It has been pointed out already that it is the fact that the perfect crystal can be represented by a single wave function at the absolute zero which explains why such crystals have zero entropy at this temperature. It was also noted that rearrangement of the identical (and indistinguishable) particles in the crystal is not considered to give rise to a new wave function. Nothing has been said about the value of the actual energy of the crystal at the absolute zero, or concerning anything that limits the crystal under consideration to one that is thermodynamically stable with respect to other crystalline forms which can be represented by a single wave function of lowest energy. Indeed, as has already been seen, metastable crystalline phases can exist at the absolute zero and according to the above discussion they will have zero entropy.

If there is random orientation frozen in at the absolute zero, there will be an entropy of mixing of the molecules with different types of orientation. Suppose there are ω_0' such orientations; this means that there are ω_0' wave functions for each molecule and $(\omega_0')^N$ wave functions for one mole of the crystal (N is the Avogadro number). Hence, the entropy in the crystal at the absolute zero is

$$S = k \ln (\omega_0')^N = R \ln \omega_0'. \tag{72.3}$$

If there are electrons with unpaired spins, the energy differences between the different orientations will always be appreciable at $T = 0$ so that the most stable orientation will result. We have seen that if there are molecules whose

[1] *Compt. rend.*, **204**, 675 (1937).

nuclei have unperturbed spin, several varieties of molecule are present depending on the relative orientation of spin in the molecules. At the absolute zero there will be an entropy of mixing due to the random distribution of these varieties in the crystal.

(73) **The Entropy of Solid Solutions at the Absolute Zero**: When solid solutions are cooled to low temperatures the processes of diffusion are so slow that near the absolute zero the molecules must remain in the fixed positions reached at higher temperatures. Thus the same entropy of solution (mixing) that existed in the solid solution at high temperatures persists down to the absolute zero. If the molecular species are sufficiently alike, these solutions may be nearly perfect and the entropy of mixing will be that calculated from the laws of ideal solution, namely that of random mixing. Looking at the matter another way, let us consider a solid solution of A and B whose mole fractions are x_A and x_B respectively. The molecules of A can equally well occupy any of $1/x_A$ positions and hence have $1/x_A$ wave functions associated with each instead of only one. There are thus $(1/x_A)^{x_A N}$ wave functions associated with the molecules of A in one mole; similarly there are $(1/x_B)^{x_B N}$ wave functions associated with the molecules of B. The total number of wave functions is consequently $(1/x_A)^{x_A N} \times (1/x_B)^{x_B N}$ instead of unity. This corresponds to an entropy of

$$S = k \ln \left[(1/x_A)^{x_A N} \times (1/x_B)^{x_B N} \right] = - R(x_A \ln x_A + x_B \ln x_B). \quad (73.1)$$

On the other hand if the solid were cooled down to the absolute zero *very slowly* the energy differences due to position would arrange the molecular species in a definite order which would correspond to a single quantum state for the crystal as a whole, namely that of lowest energy. The entropy of such a crystal would be zero. It should be noted that the type of solid solution which would behave in such a manner as to produce zero entropy at the absolute zero would of necessity obey either the Einstein-Bose or Fermi-Dirac distribution laws. Gravity is an example of a force creating appreciable energy differences with molecules of different mass. At the absolute zero the crystal would separate into an upper half of the lighter type of molecule and a lower half of the heavier *if the molecules were free to move*. Practically such a situation is impossible. An actual solid solution, then, will have a residual entropy at the absolute zero which will be given by (73.1).

Eastman and Milner [1] studied the entropy of a solid solution of silver chloride (mole fraction 0.27) and silver bromide (mole fraction 0.73) From the third law they found an entropy 1.03 ± 0.02 cal./deg./mole lower than from cell measurements; this difference is the entropy of mixing for which the calculated value using equation (73.1) is 1.16 cal./deg./mole. This agreement provides one of the best confirmations of the basic ideas concerning the Third Law of Thermodynamics.

[1] *J. Chem. Phys.*, **1**, 444 (1933).

(74) The Entropy of Gases and Mobile Liquids at the Absolute Zero: At the absolute zero, a gaseous system or a mobile liquid system would be represented by a single wave function or quantum state except for nuclear spin effects, and hence has zero entropy. It is interesting to see how the wave functions (quantum states) for the individual molecules give rise to such a situation.

Gases and mobile liquids may be treated in the same way. Either the Einstein-Bose or the Fermi-Dirac distribution applies depending on the nature of the molecules. In both cases we use the relation

$$S = k \ln P, \tag{74.1}$$

where P is the expression for the number of microscopic states (number of wave functions). All of the n molecules are in the state of lowest allowed energy; hence,

$$n_1 = n \qquad \text{while} \qquad n_2 = n_3 = \cdots n_i = \cdots n_\alpha = 0.$$

For the Einstein-Bose distribution there is only one state of the molecules of lowest energy for any one nuclear spin wave function. In other words for the Einstein-Bose distribution $p_1 = 1$. For the Fermi-Dirac distribution p_1 must be equal to or greater than n_1 in order that each of the states of lowest energy shall have a different wave function. We shall take $p_1 = n_1 = n$, so that for the two cases:

Einstein-Bose

$$S = k \ln P = k \ln \Pi \left[\frac{(n_k + p_k - 1)!}{n_k! \, (p_k - 1)!} \right] = k \ln \frac{n!}{n! \, 0!} = k \ln 1 = 0. \tag{74.2}$$

Fermi-Dirac

$$S = k \ln P = k \ln \Pi \left[\frac{p_k!}{n_k! \, (p_k - n_k)!} \right] = k \ln \frac{n!}{n! \, 0!} = k \ln 1 = 0. \tag{74.3}$$

Where there is no degeneracy of the lowest level, if the Fermi-Dirac distribution law applies, each molecule must be in a slightly different lowest energy level with a different wave function for each: that is, $n_1 = 1$, $n_2 = 1$, $\cdots$, $n_n = 1$ and $p_k = 1$. Under these conditions,

$$S = k \ln P = k \ln \Pi \frac{1!}{1! \, 0!} = k \ln 1 = 0. \tag{74.4}$$

It is of interest to examine what happens to the heat capacity and entropy of a gas as it approaches this state of zero entropy. We have already seen that the heat capacity of a highly degenerate Fermi-Dirac gas is given by

$$C_v = n \frac{\pi^2 m k^2}{h^2} \left(\frac{4\pi V p_s}{3n} \right)^{2/3} T, \tag{74.5}$$

so that the heat capacity approaches zero as T approaches zero. For low temperatures an expression for the entropy of a Fermi-Dirac gas is simply obtained by use of the general relation

$$F = - nkT\alpha, \tag{74.6}$$

$$S = \frac{E + PV}{T} + nk\alpha. \tag{74.7}$$

According to (27.11) for large negative values of α,

$$\alpha = - \left(\frac{3\sqrt{\pi}}{4} y \right)^{2/3} \left\{ 1 - \frac{\pi^2}{12} \left(\frac{4}{3\sqrt{\pi y}} \right)^{4/3} \cdots \right\} \tag{74.8}$$

with y given by (26.13). Noting that PV is equal to $\frac{2}{3}E$ as can be seen from equation (26.22),

$$S = \frac{5}{3} \cdot \frac{E}{T} + nk\alpha \tag{74.9}$$

with E given by (27.3).

For very large values of y (very large negative α)

$$\alpha \rightarrow - \left(\frac{3\sqrt{\pi}}{4} y \right)^{2/3}. \tag{74.10}$$

Moreover, since

$$V(\alpha, \tfrac{3}{2}) = \frac{8(-\alpha)^{5/2}}{15\pi^{1/2}} \rightarrow \frac{2}{5} \left(\frac{3\sqrt{\pi}}{4} y \right)^{2/3} y, \tag{74.11}$$

it follows that

$$\frac{5}{3} \cdot \frac{E}{T} = \tfrac{5}{2} nk \frac{V(\alpha, \tfrac{3}{2})}{y} \rightarrow nk \left(\frac{3\sqrt{\pi}}{4} y \right)^{2/3} = - nk\alpha \tag{74.12}$$

and hence the entropy approaches zero asymptotically.

The corresponding treatment for an Einstein-Bose gas has been carried out by F. London.[1] It will be noted that equations (26.27) and (26.28) give the energy of an Einstein-Bose gas in terms of y defined by (26.13) and which may have any positive value. According to (26.15) and (26.24), however

$$y \equiv \frac{nh^3}{Vp_s(2\pi mkT)^{3/2}} = U(\alpha, \tfrac{1}{2}) = e^{-\alpha} + \frac{e^{-2\alpha}}{2^{3/2}} + \frac{e^{-3\alpha}}{3^{3/2}} \cdot \tag{74.13}$$

The right-hand side has a maximum value for $\alpha = 0$, since negative values of α are inadmissible in equation (22.14) as they would lead to a negative number of molecules in low energy states. The difficulty is due to the expression

[1] *Phys. Rev.*, **54**, 947 (1938).

(26.9) used for the number of states, p, based on a continuous series of energy values and which gives an *a priori* probability of zero to the state of zero energy. This approximation is satisfactory at temperatures where most of the molecules are in high energy states but not at very low temperatures where the population of low energy states is high.

The temperature, T_0, for which

$$y = y_0 = \frac{nh^3}{V p_s (2\pi mk T_0)^{3/2}} = 1 + \frac{1}{2^{3/2}} + \frac{1}{3^{3/2}} + \cdots = 2.612 \quad (74.14)$$

is on the threshold of the high temperature region in which (26.27) and (26.28) will hold.

The difficulty can be avoided by separating out the states of low energy (say about the ten lowest). The energy levels of the free particle in a cubical container with sides of length L are

$$\epsilon_{k,l,m} = \frac{h^2 \rho^2}{2mL^2} = 2.612^{2/3}\pi k T_0 \left(\frac{p_s}{n}\right)^{2/3} \rho^2 = 5.97 \left(\frac{p_s}{n}\right)^{2/3} k T_0 \rho^2 \quad (74.15)$$

with

$$\rho^2 = k^2 + l^2 + m^2, \quad (74.16)$$

where k, l and m are integers. We separate out the group of p_0 levels with

$$\rho \gtreqless \rho_0; \qquad \epsilon \gtreqless \epsilon_0 = \frac{h^2 \rho_0^2}{2mL^2}. \quad (74.17)$$

According to (26.9) the average energy of this group of levels is given by

$$\bar{\epsilon}_0 = \frac{\displaystyle\int_0^{\epsilon_0} \epsilon^{3/2} d\epsilon}{\displaystyle\int_0^{\epsilon_0} \epsilon^{1/2} d\epsilon} = \tfrac{3}{5}\epsilon_0. \quad (74.18)$$

Thus referring to (26.12)

$$n = \frac{p_0}{e^{\beta\epsilon_0 + \alpha} - 1} + \frac{n}{y\Gamma(\tfrac{1}{2} + 1)} \int_{\beta\epsilon_0}^{\infty} \frac{z^{1/2} dz}{e^{z+\alpha} - 1}, \quad (74.19)$$

noting that

$$y \equiv \frac{nh^3}{V p_s (2\pi mk T)^{3/2}} = 2.612 \left(\frac{T_0}{T}\right)^{3/2}, \quad (74.20)$$

$$n = \frac{p_0}{e^{\beta\epsilon_0 + \alpha} - 1} + \frac{2n}{2.612\pi^{1/2}} \left(\frac{T}{T_0}\right)^{3/2} \int_{\beta\epsilon_0}^{\infty} \frac{z^{1/2} dz}{e^{z+\alpha} - 1}. \quad (74.21)$$

Then substituting

$$\alpha' = \beta\bar{\epsilon}_0 + \alpha = \tfrac{3}{5}\beta\epsilon_0 + \alpha, \quad (74.22)$$

when $\alpha' \lessgtr 0$ in order that the first term of (74.21) be positive (it should be noted that $\beta\epsilon_0$ is always very small by definition),

$$1 = \frac{p_0/n}{e^{\alpha'} - 1} + \left(\frac{T}{T_0}\right)^{3/2} \frac{2}{2.612\pi^{1/2}} \int_{\beta\epsilon_0}^{\infty} \frac{z^{1/2}dz}{e^{z+\alpha'-(3\beta\epsilon_0/5)} - 1} . \tag{74.23}$$

For $T > T_0$: In this case α' (approximately equal to α) turns out to be of the order of magnitude of unity (see 26.29). Thus the first term on the right of (74.23) is of the order of magnitude of $1/n$ and may be neglected compared with the second term. Further $3\beta\epsilon_0/5$ may be neglected compared with α'. Since the lower limit of the integral in the second term may be taken as zero, (74.23) is equivalent to (26.10) so that (26.28) is valid for the total energy and (26.27) for the pressure of the gas; or

$$\left(\frac{T_0}{T}\right)^{3/2} = \frac{U(\alpha', \frac{1}{2})}{U(0, \frac{1}{2})} = \frac{U(\alpha, \frac{1}{2})}{U(0, \frac{1}{2})} . \tag{74.24}$$

For $T < T_0$: The second term of the right-hand side of (74.23) must always be smaller than $(T/T_0)^{3/2}$ since the upper limit of the coefficient is unity. For $T < T_0$ the term is therefore smaller than unity and the first term must make up for the difference. Since the numerator is very small (of the order of $1/n$) the denominator must also be small and α' must be close to zero; therefore α' may be neglected compared with $3\beta\epsilon_0/5$ in the second term and $e^{\alpha'}$ may be represented by the first two terms of its power expansion. Under these conditions

$$1 = \frac{p_0}{n\alpha'} + \left(\frac{T}{T_0}\right)^{3/2} \frac{2}{2.612\pi^{1/2}} \int_{\beta\epsilon_0}^{\infty} \frac{z^{1/2}dz}{e^{z-3\beta\epsilon_0/5} - 1}$$
$$= \frac{p_0}{n\alpha'} + \left(\frac{T}{T_0}\right)^{3/2} [1 - 0.173(\beta\epsilon_0)^{1/2} + \cdots] \tag{74.25}$$

or

$$\alpha' = \frac{p_0}{n}\left[1 - \left(\frac{T}{T_0}\right)^{3/2}\{1 - 0.173(\beta\epsilon_0)^{1/2} + \cdots\}\right]^{-1} . \tag{74.26}$$

Remembering that α' is very small, the number of particles in the p_0 lowest states is

$$n_0 = \frac{p_0}{e^{\alpha'} - 1} = \frac{p_0}{\alpha'}$$
$$= n[1 - (T/T_0)^{3/2}\{1 - 0.173(\beta\epsilon_0)^{1/2} + \cdots\}]$$
$$= n[1 - (T/T_0)^{3/2}] + 0.422p_0 n^{2/3}p_s^{1/3}T/T_0 + \cdots. \tag{74.27}$$

It is to be noted that to a first approximation the second term in (74.27) can be neglected and, therefore, that the number of molecules in the group of lowest states chosen is independent of p_0, which determines the upper limit of energy

of the group. Thus the number of molecules, n_0, in the p_0 lowest states is independent of p_0 and

$$n_0 = n[1 - (T/T_0)^{3/2}] \qquad (74.28)$$

can be taken to represent the number of molecules in the *single* lowest state accordingly. Now applying (22.14) to the lowest state

$$n_0 = \frac{p_s}{e^\alpha - 1} \approx \frac{p_s}{\alpha}$$

$$\alpha = \frac{p_s}{n_0} = \frac{p_s}{n[1 - (T/T_0)^{3/2}]} \ . \qquad (74.29)$$

The number of molecules in any of the other lowest states is therefore given by

$$n_k = \frac{p_s}{e^{5.97(p_s/n)^{2/3}(T_0/T)^{2}+\alpha} - 1} = \frac{p_s}{\alpha\left[1 + 5.97\left(\frac{p_s}{n}\right)^{2/3}\left(\frac{T_0}{T}\right)\left(\frac{\rho^2}{\alpha}\right)\right]}$$

$$= \frac{n(1 - T_0/T)^{3/2}}{1 + 5.97\left(\frac{n}{p_s}\right)^{1/3}\left(\frac{T_0}{T}\right)\left[1 - \left(\frac{T_0}{T}\right)^{1/2}\right](k^2 + l^2 + m^2)} \ . \qquad (74.30)$$

It is evident that for $T \leqslant T_0$, α as defined by (74.29) approaches zero for very large n (n/V constant) while according to (74.13) and (74.24) for $T \geqslant T_0$, α is a finite function of T. It is found that α has a discontinuous second derivative at $T = T_0$; the temperature T_0 represents a *condensation point* in the distribution as will be seen from the following discussion.

Above T_0 the energy is represented by (26.28) which after writing $y = 2.612(T_0/T)^{3/2}$ becomes

$$E_+ = \frac{3RT}{2}\{1 - 0.462(T_0/T)^{3/2} - 0.0225(T_0/T)^3 - 0.0114(T_0/T)^{9/2}\}. \qquad (74.31)$$

Below T_0 the energy is

$$E_- = \sum \epsilon_k n_k = \int_0^\infty \frac{2\pi V p_s}{h^3}(2m)^{3/2}\frac{\epsilon^{3/2}d\epsilon}{e^{\beta\epsilon} - 1}$$

$$= \int_0^\infty \frac{2\pi V p_s}{h^3}(2m)^{3/2}(kT)^{5/2}\frac{z^{3/2}dz}{e^z - 1} \qquad (74.32)$$

or

$$E_- = {}^{3}_{2}RT\left(\frac{T}{T_0}\right)^{3/2}\frac{\zeta(2.5)}{\zeta(1.5)}, \qquad (74.33)$$

where

$$\zeta(k) = \frac{1}{\Gamma(k)}\int_0^\infty \frac{z^{k-1}}{e^z - 1}dz; \qquad \zeta(2.5) = 1.341; \qquad \zeta(1.5) = 2.612.$$

Thus

$$E_- = {}^3_2 0.514RT\left(\frac{T}{T_0}\right)^{3/2}, \tag{74.34}$$

$$= {}^3_2 0.514RCT^{5/2}V \tag{74.35}$$

with

$$C = \frac{2.612}{n}\left(\frac{2\pi mk}{h^2}\right)^{3/2} \approx {}^1_{153}\ \text{for helium.}$$

The two branches E_+ and E_- are continuous at $T = T_0$ with a continuous derivative. The second derivative is, however, discontinuous, and C_v exhibits a break.

The expressions for C_r are

$$C_{v+} = {}^3_2 R\{1 + 0.231(T_0/T)^{3/2}$$
$$+ 0.045(T_0/T)^3 + 0.040(T_0/T)^{9/2} + \cdots\}, \tag{74.36}$$

$$C_{v-} = {}^{15}_4 0.514R(T/T_0)^{3/2}. \tag{74.37}$$

Thus it is seen that at very low temperatures C_v is given by (74.37) which predicts zero heat capacity at the absolute zero. Figure 15 is a graph of C_v plotted against T/T_0; the break in the heat capacity at $T/T_0 = 1$ is quite apparent.

Finally for the pressure at temperatures below T_0

$$P_- = \frac{2}{3}\cdot\frac{E_-}{V} = 0.514RCT^{5/2}. \tag{74.38}$$

Evidently below the temperature T_0 the pressure is independent of the density and this temperature can be considered as a temperature of condensation in momentum space. The condensation has no meaning with respect to coordinate space. Since the energy of the particles is zero in the lowest state they must be regarded as having zero momentum and therefore, according to the principle of uncertainty, the position of the particles that condense to the lowest state cannot be known except to say that they lie somewhere in the container.

Unfortunately at ordinary gas densities T_0 occurs at temperatures where even helium would be a liquid. However it is interesting to apply these results to helium gas for densities equal to those in the liquid and see if the results obtained have any parallel in the behavior of the liquid at low temperatures.

The entropy at temperatures below T_0 is given on a molal basis by

$$S = \frac{5}{3}\cdot\frac{E}{T} + Nk\alpha = \frac{5}{3}\cdot\frac{E}{T} + R\ln\left(\frac{p_s}{n_0}+1\right). \tag{74.39}$$

But at temperatures where almost all the molecules are in the lowest state p_s/n_0

is negligible compared with unity and

$$S = \frac{5}{3} \cdot \frac{E}{T} = {}^{5}{}_{2}0.514R\left(\frac{T}{T_0}\right)^{3/2} = 1.285R\left(\frac{T}{T_0}\right)^{3/2}, \qquad (74.40)$$

so that at $T = 0$ the entropy is zero.
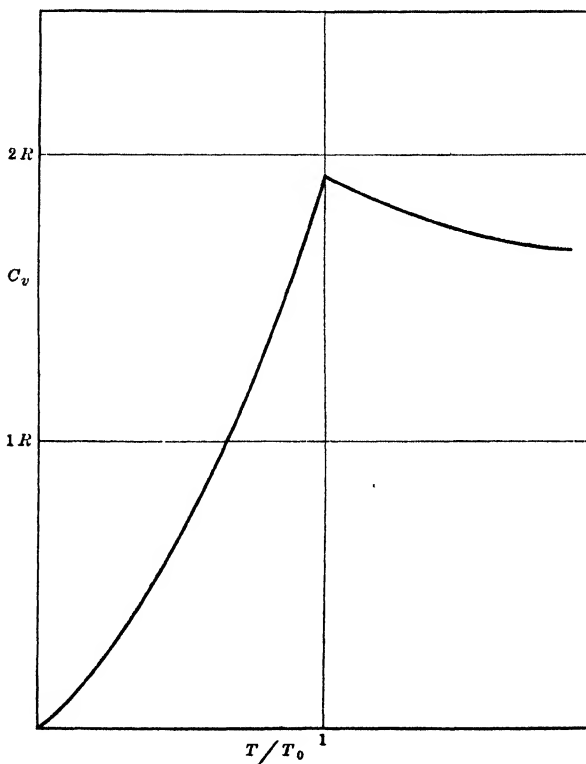
FIG. 15.   Specific Heat (C_v) of an Ideal Bose-Einstein Gas

Liquid helium has a second order transition known as the *lambda point* between 1.2° K and 2.5° K; liquid helium I is stable above and liquid helium II below it.   F. London [1] has suggested that this transition (the only liquid transition known) is of a similar nature to the condensation effect occurring in the neighborhood of T_0 for an Einstein-Bose gas.   For helium gas with an atomic volume of 27.6 cc. (equal to that of the liquid at the *lambda point*) T_0 calculated by (74.14) is 3.14° K.   The accurate treatment of the problem requires a

[1] *Phys. Rev.*, **54**, 947 (1938); *J. Phys. Chem.*, **43**, 49 (1939).

knowledge of the energy levels in the liquid.   F. London assumes that part of the wave functions are similar to those giving rise to lattice vibrations in a crystal while the others are like those attributed to free electrons in metals. The curve in Fig. 16 shows his calculated heat capacities (C_v/R), plotted against T/T_0, in the neighborhood of the lambda point; the circles are the experimental points.[1]
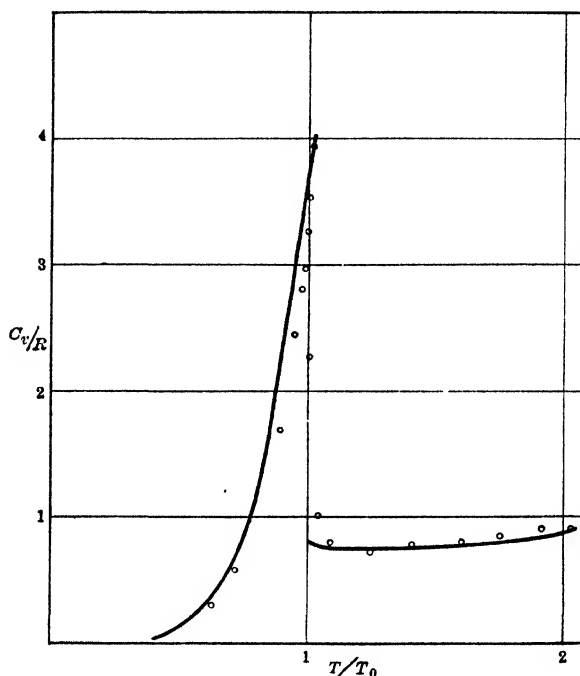
Fig. 16.   Specific Heat (C_v) for Bose-Einstein Statistics   The circles give the experimental values for helium

The fact that helium II obeys the T^3 law at very low temperatures indicates that the very lowest energy levels are similar to those in a crystal.   According to the entropy diagram of Keesom and Keesom the entropy of helium II (the form of liquid stable below the lambda point) is only a little higher than that of the solid and approaches it as the temperature is lowered.

It should be noted that, while there is no doubt that gases and mobile liquids will have zero entropy at the absolute zero, the corresponding order is not one in space.   The single lowest quantum state, in which all the particles are to be found corresponds to zero momentum and hence, according to the principle

[1] Keesom and Clusius, *Leiden Comm.*, 219e (1932); Keesom, W. H. and Keesom, A. P., Leiden Comm., 221d (1932); *Physica*, 2, 557 (1935); 3, 359 (1936).

of uncertainty, to an unknown position. The situation is the direct opposite of that existing in a crystal. The important point in both cases is that the system is in a single quantum state.

(75) **The Entropy of Glasses at the Absolute Zero:** A glass may be considered as a number of localized microscopic liquid regions randomly distributed. The entropy of the glass at the absolute zero will be the entropy of mixing of these regions and will be considerably larger than zero. This has been verified for crystalline glycerol glass by Gibson and Giauque [1] and by Simon and Lange [2] The entropy in glycerol glass at the absolute zero is 4.6 cal./deg./mole while that for ethyl alcohol glass is 2.6 cal./deg./mole.[3] The lower value for ethyl alcohol is perhaps due to the lower temperature at which it becomes glassy. For the lower temperature at which the degrees of freedom are frozen there are fewer wave functions (quantum states) among which the system is distributed, other things being equal, and so the number of randomly distributed microscopic regions is less.

[1] *J. Am. Chem. Soc.*, **45**, 93 (1923).

[2] *Z. Physik*, **38**, 227 (1926).

[3] Kelley, *J. Am. Chem. Soc.*, **51**, 779 (1929).

APPENDIX I

Harmonic Oscillator Contributions

The contribution (in cal./deg./mole) of a fundamental vibration frequency ν (wave numbers in cm.$^{-1}$) to the heat capacity, heat content, and free energy are given as a function of ν/T.

$$\frac{F - E_0}{T} = R \ln (1 - e^{-x}),$$

$$C = \frac{Rx^2}{2(\cosh x - 1)},$$

$$\frac{E - E_0}{T} = \frac{Rxe^{-x}}{(1 - e^{-x})},$$

$$x = \frac{hc\nu}{kT}.$$

The contribution to the entropy is given by $S = \dfrac{E - E_0}{T} - \dfrac{F - E_0}{T}$. All constants are from the latest values of Birge (1941). This table was obtained by Dr. E. B. Wilson, Jr., by interpolation from unpublished calculations of Dr. H. L. Johnston, and has been corrected to the basis of the new constants by Dr. S. C. Schumann and Mr. M. L. Schwartz of The Pennsylvania State College.

v/T	C	$\dfrac{E-E_0}{T}$	$-\dfrac{(F-E_0)}{T}$	v/T	C	$\dfrac{E-E_0}{T}$	$-\dfrac{(F-E_0)}{T}$
0.10	1.9834	1.8473	3.9942	0.55	1.8863	1.3034	1.2001
0.11	1.9827	1.8338	3.8186	0.56	1.8827	1.2929	1.1766
0.12	1.9819	1.8203	3.6596	0.57	1.8791	1.2823	1.1539
0.13	1.9810	1.8068	3.5143	0.58	1.8754	1.2719	1.1316
0.14	1.9801	1.7935	3.3807	0.59	1.8718	1.2616	1.1099
0.15	1.9791	1.7801	3.2572	0.60	1.8680	1.2513	1.0887
0.16	1.9780	1.7670	3.1428	0.61	1.8641	1.2411	1.0681
0.17	1.9768	1.7538	3.0361	0.62	1.8602	1.2308	1.0481
0.18	1.9756	1.7407	2.9362	0.63	1.8562	1.2207	1.0284
0.19	1.9744	1.7276	2.8424	0.64	1.8522	1.2107	1.0093
0.20	1.9731	1.7147	2.7542	0.65	1.8481	1.2007	0.9905
0.21	1.9717	1.7018	2.6710	0.66	1.8441	1.1908	0.9722
0.22	1.9703	1.6890	2.5920	0.67	1.8398	1.1810	0.9545
0.23	1.9687	1.6763	2.5142	0.68	1.8357	1.1711	0.9370
0.24	1.9671	1.6636	2.4662	0.69	1.8315	1.1614	0.9200
0.25	1.9655	1.6510	2.3786	0.70	1.8272	1.1517	0.9033
0.26	1.9638	1.6384	2.3140	0.71	1.8227	1.1420	0.8870
0.27	1.9620	1.6260	2.2525	0.72	1.8184	1.1325	0.8713
0.28	1.9601	1.6135	2.1935	0.73	1.8140	1.1230	0.8557
0.29	1.9583	1.6012	2.1372	0.74	1.8093	1.1135	0.8405
0.30	1.9563	1.5889	2.0831	0.75	1.8047	1.1041	0.8256
0.31	1.9542	1.5767	2.0311	0.76	1.8002	1.0948	0.8110
0.32	1.9521	1.5645	1.9813	0.77	1.7955	1.0856	0.7968
0.33	1.9500	1.5525	1.9333	0.78	1.7908	1.0764	0.7828
0.34	1.9478	1.5404	1.8872	0.79	1.7863	1.0674	0.7692
0.35	1.9454	1.5285	1.8427	0.80	1.7813	1.0582	0.7558
0.36	1.9430	1.5167	1.7998	0.81	1.7765	1.0492	0.7437
0.37	1.9406	1.5048	1.7584	0.82	1.7716	1.0403	0.7299
0.38	1.9381	1.4931	1.7185	0.83	1.7667	1.0314	0.7174
0.39	1.9356	1.4814	1.6799	0.84	1.7618	1.0226	0.7052
0.40	1.9330	1.4698	1.6425	0.85	1.7568	1.0138	0.6931
0.41	1.9303	1.4583	1.6063	0.86	1.7517	1.0050	0.6812
0.42	1.9275	1.4468	1.5713	0.87	1.7466	0.9964	0.6697
0.43	1.9247	1.4354	1.5374	5.88	1.7415	0.9878	0.6583
0.44	1.9218	1.4240	1.5045	0.89	1.7364	0.9793	0.6473
0.45	1.9188	1.4128	1.4726	0.90	1.7312	0.9708	0.6363
0.46	1.9159	1.4016	1.4416	0.91	1.7259	0.9620	0.6256
0.47	1.9128	1.3904	1.4117	0.92	1.7206	0.9541	0.6151
0.48	1.9097	1.3793	1.3826	0.93	1.7154	0.9458	0.6049
0.49	1.9066	1.3682	1.3543	0.94	1.7099	0.9377	0.5948
0.50	1.9033	1.3573	1.3267	0.95	1.7045	0.9295	0.5848
0.51	1.9001	1.3464	1.3001	0.96	1.6991	0.9212	0.5751
0.52	1.8966	1.3354	1.2741	0.97	1.6935	0.9132	0.5657
0.53	1.8933	1.3248	1.2488	0.98	1.6882	0.9051	0.5563
0.54	1.8898	1.3140	1.2242	0.99	1.6826	0.8971	0.5471

ν/T	C	$\dfrac{E-E_0}{T}$	$\dfrac{-(F-E_0)}{T}$	ν/T	C	$\dfrac{E-E_0}{T}$	$\dfrac{-(F-E_0)}{T}$
1.00	1.6770	0.8893	0.5382	1.45	1.3999	0.5879	0.2636
1.01	1.6714	0.8815	0.5294	1.46	1.3934	0.5823	0.2595
1.02	1.6658	0.8737	0.5208	1.47	1.3868	0.5768	0.2556
1.03	1.6601	0.8659	0.5123	1.48	1.3802	0.5713	0.2518
1.04	1.6544	0.8582	0.5040	1.49	1.3736	0.5658	0.2471
1.05	1.6487	0.8507	0.4959	1.50	1.3671	0.5604	0.2441
1.06	1.6429	0.8430	0.4877	1.51	1.3605	0.5550	0.2404
1.07	1.6371	0.8355	0.4800	1.52	1.3538	0.5493	0.2367
1.08	1.6312	0.8281	0.4722	1.53	1.3473	0.5445	0.2332
1.09	1.6254	0.8207	0.4647	1.54	1.3406	0.5392	0.2297
1.10	1.6196	0.8133	0.4572	1.55	1.3340	0.5340	0.2262
1.11	1.6137	0.8060	0.4499	1.56	1.3274	0.5288	0.2227
1.12	1.6077	0.7988	0.4426	1.57	1.3208	0.5238	0.2193
1.13	1.6017	0.7916	0.4357	1.58	1.3143	0.5187	0.2161
1.14	1.5957	0.7845	0.4287	1.59	1.3077	0.5138	0.2129
1.15	1.5897	0.7774	0.4218	1.60	1.3010	0.5088	0.2097
1.16	1.5837	0.7703	0.4151	1.61	1.2943	0.5039	0.2065
1.17	1.5776	0.7634	0.4086	1.62	1.2878	0.4988	0.2034
1.18	1.5715	0.7564	0.4021	1.63	1.2812	0.4942	0.2004
1.19	1.5653	0.7495	0.3957	1.64	1.2746	0.4893	0.1974
1.20	1.5592	0.7427	0.3894	1.65	1.2680	0.4847	0.1944
1.21	1.5531	0.7359	0.3832	1.66	1.2613	0.4799	0.1914
1.22	1.5468	0.7292	0.3773	1.67	1.2547	0.4753	0.1885
1.23	1.5406	0.7225	0.3713	1.68	1.2481	0.4706	0.1858
1.24	1.5343	0.7159	0.3656	1.69	1.2415	0.4659	0.1830
1.25	1.5281	0.7093	0.3598	1.70	1.2349	0.4613	0.1802
1.26	1.5217	0.7027	0.3542	1.71	1.2283	0.4568	0.1775
1.27	1.5156	0.6963	0.3486	1.72	1.2217	0.4523	0.1749
1.28	1.5091	0.6898	0.3432	1.73	1.2151	0.4478	0.1723
1.29	1.5030	0.6834	0.3379	1.74	1.2086	0.4435	0.1698
1.30	1.4966	0.6771	0.3326	1.75	1.2018	0.4391	0.1672
1.31	1.4902	0.6708	0.3275	1.76	1.1952	0.4348	0.1647
1.32	1.4839	0.6646	0.3225	1.77	1.1887	0.4304	0.1622
1.33	1.4774	0.6585	0.3175	1.78	1.1822	0.4262	0.1599
1.34	1.4710	0.6523	0.3126	1.79	1.1756	0.4219	0.1575
1.35	1.4646	0.6462	0.3078	1.80	1.1690	0.4177	0.1551
1.36	1.4583	0.6402	0.3030	1.81	1.1625	0.4135	0.1528
1.37	1.4520	0.6342	0.2983	1.82	1.1559	0.4096	0.1505
1.38	1.4455	0.6283	0.2937	1.83	1.1493	0.4053	0.1484
1.39	1.4390	0.6223	0.2893	1.84	1.1428	0.4011	0.1461
1.40	1.4324	0.6164	0.2848	1.85	1.1363	0.3972	0.1440
1.41	1.4259	0.6107	0.2804	1.86	1.1298	0.3932	0.1418
1.42	1.4194	0.6049	0.2761	1.87	1.1233	0.3893	0.1397
1.43	1.4129	0.5998	0.2719	1.88	1.1167	0.3855	0.1377
1.44	1.4065	0.5935	0.2677	1.89	1.1102	0.3816	0.1356

ν/T	C	$\dfrac{E-E_0}{T}$	$-\dfrac{(F-E_0)}{T}$	ν/T	C	$\dfrac{E-E_0}{T}$	$-\dfrac{(F-E_0)}{T}$
1.90	1.1038	0.3777	0.1336	2.70	0.6429	0.1622	0.04131
1.91	1.0973	0.3739	0.1316	2.72	0.6332	0.1587	0.04014
1.92	1.0909	0.3701	0.1297	2.74	0.6236	0.1553	0.03901
1.93	1.0845	0.3665	0.1278	2.76	0.6140	0.1519	0.03788
1.94	1.0780	0.3627	0.1259	2.78	0.6046	0.1483	0.03679
1.95	1.0716	0.3591	0.1240	2.80	0.5953	0.1454	0.03572
1.96	1.0653	0.3554	0.1222	2.82	0.5862	0.1422	0.03471
1.97	1.0589	0.3518	0.1205	2.84	0.5771	0.1391	0.03371
1.98	1.0525	0.3482	0.1187	2.86	0.5680	0.1361	0.03275
1.99	1.0461	0.3446	0.1169	2.88	0.5591	0.1331	0.03181
2.00	1.0398	0.3412	0.1152	2.90	0.5502	0.1301	0.03089
2.02	1.0272	0.3342	0.1118	2.92	0.5417	0.1272	0.03003
2.04	1.0146	0.3275	0.1085	2.94	0.5331	0.1244	0.02917
2.06	1.0020	0.3208	0.1054	2.96	0.5246	0.1216	0.02834
2.08	0.9897	0.3142	0.1023	2.98	0.5163	0.1189	0.02752
2.10	0.9772	0.3077	0.0992	3.00	0.5080	0.1162	0.02673
2.12	0.9649	0.3014	0.09640	3.05	0.4876	0.1099	0.02486
2.14	0.9526	0.2952	0.09362	3.10	0.4680	0.1038	0.02311
2.16	0.9405	0.2891	0.09091	3.15	0.4489	0.0981	0.02150
2.18	0.9284	0.2832	0.08828	3.20	0.4305	0.0927	0.02000
2.20	0.9161	0.2773	0.08576	3.25	0.4127	0.0875	0.01861
2.22	0.9041	0.2716	0.08326	3.30	0.3956	0.0826	0.01731
2.24	0.8921	0.2659	0.08084	3.35	0.3787	0.0780	0.01608
2.26	0.8799	0.2605	0.07850	3.40	0.3627	0.0736	0.01498
2.28	0.8682	0.2551	0.07622	3.45	0.3471	0.0696	0.01393
2.30	0.8570	0.2497	0.07402	3.50	0.3323	0.0656	0.01297
2.32	0.8455	0.2445	0.07189	3.55	0.3177	0.0619	0.01207
2.34	0.8339	0.2394	0.06982	3.60	0.3038	0.0584	0.01124
2.36	0.8225	0.2344	0.06780	3.65	0.2903	0.0550	0.01045
2.38	0.8112	0.2295	0.06585	3.70	0.2775	0.0519	0.00972
2.40	0.8000	0.2246	0.06395	3.75	0.2651	0.0489	0.00904
2.42	0.7885	0.2198	0.06213	3.80	0.2532	0.0461	0.00842
2.44	0.7778	0.2151	0.06032	3.85	0.2417	0.0435	0.00783
2.46	0.7669	0.2106	0.05859	3.90	0.2307	0.0410	0.00729
2.48	0.7560	0.2061	0.05690	3.95	0.2201	0.0387	0.00678
2.50	0.7453	0.2017	0.05526	4.00	0.2099	0.0364	0.00631
2.52	0.7346	0.1974	0.05370	4.10	0.1907	0.0322	0.00547
2.54	0.7240	0.1932	0.05217	4.20	0.1732	0.0286	0.00473
2.56	0.7135	0.1891	0.05065	4.30	0.1571	0.0253	0.00409
2.58	0.7031	0.1850	0.04919	4.40	0.1424	0.0225	0.00354
2.60	0.6928	0.1810	0.04778	4.50	0.1286	0.0200	0.00306
2.62	0.6826	0.1771	0.04640	4.60	0.1166	0.0176	0.00265
2.64	0.6725	0.1732	0.04507	4.70	0.1054	0.0156	0.00230
2.66	0.6625	0.1695	0.04379	4.80	0.0952	0.0138	0.00199
2.68	0.6527	0.1656	0.04253	4.90	0.0859	0.0122	0.00173

ν/T	c	$\dfrac{E-E_0}{T}$	$\dfrac{-(F-E_0)}{T}$	ν/T	c	$\dfrac{E-E_0}{T}$	$\dfrac{-(F-E_0)}{T}$
5.00	0.0775	0.01074	0.00150	7.50	0.00474	0.000441	0.0000427
5.10	0.0697	0.00948	0.001290	7.60	0.00423	0.0003868	0.0000369
5.20	0.0628	0.00836	0.001116	7.70	0.00376	0.0003497	0.0000320
5.30	0.0563	0.00740	0.000965	7.80	0.00332	0.0002979	0.0000278
5.40	0.0506	0.00652	0.000837	7.90	0.00298	0.0002618	0.0000241
5.50	0.0454	0.00575	0.000727	8.00	0.00265	0.0002292	0.0000209
5.60	0.0409	0.00507	0.000629	8.10	0.00234	0.0002008	0.0000181
5.70	0.0367	0.00447	0.000545	8.20	0.00208	0.0001759	0.0000156
5.80	0.0330	0.00393	0.000472	8.30	0.00185	0.0001542	0.0000135
5.90	0.0295	0.00347	0.000409	8.40	0.00164	0.0001352	0.0000117
6.00	0.0265	0.00305	0.000353	8.50	0.00145	0.0001187	0.0000101
6.10	0.0236	0.00269	0.000306	8.60	0.00129	0.0001038	0.0000088
6.20	0.0212	0.00236	0.000266	8.70	0.00113	0.0000908	0.0000077
6.30	0.0189	0.00208	0.000231	8.80	0.00101	0.0000795	0.0000067
6.40	0.0169	0.00183	0.000200	8.90	0.00089	0.0000696	0.0000058
6.50	0.0151	0.00161	0.000173	9.00	0.000792	0.0000610	0.0000050
6.60	0.0134	0.00142	0.000151	9.10	0.000701	0.0000535	0.0000043
6.70	0.0120	0.00125	0.000131	9.20	0.000620	0.0000466	0.0000037
6.80	0.0107	0.00110	0.000114	9.30	0.000549	0.0000408	0.0000032
6.90	0.00960	0.000962	0.0000993	9.40	0.000486	0.0000357	0.0000028
7.00	0.00852	0.000845	0.0000865	9.50	0.000431	0.0000312	0.0000024
7.10	0.00758	0.000742	0.0000750	9.60	0.000380	0.0000273	0.0000021
7.20	0.00674	0.000651	0.0000651	9.70	0.000335	0.0000239	0.0000018
7.30	0.00600	0.000571	0.0000565	9.80	0.000297	0.0000209	0.0000016
7.40	0.00534	0.000502	0.0000491	9.90	0.000262	0.0000184	0.0000014
				10.00	0.000232	0.0000161	0.0000012

APPENDIX II [*]

THERMODYNAMIC FUNCTIONS FOR MOLECULES WITH RESTRICTED INTERNAL ROTATION

$$V = \tfrac{1}{2}V_0(1 - \cos n\phi).$$

The functions (in cal./deg./mole) are tabulated with V in cal./mole and I in c.g.s. units per molecule.

TABLE A

E/T

V/RT	$10^{-36}n^2/IV$								
	0	1	2	4	8	16	32	64	128
0.0	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
0.5	1.43	1.36	1.34	1.32	1.28	1.25	1.19	1.12	1.04
1.0	1.24	1.64	1.60	1.55	1.48	1.41	1.30	1.17	1.02
2.0	2.09	1.93	1.86	1.76	1.63	1.47	1.26	1.05	0.89
3.0	2.18	1.95	1.86	1.73	1.54	1.34	1.07	0.84	
4.0	2.19	1.87	1.74	1.58	1.37	1.12	0.85	0.64	
5.0	2.17	1.78	1.62	1.42	1.20	0.92	0.66		
6.0	2.14	1.67	1.49	1.27	1.02	0.73	0.49		
7.0	2.10	1.56	1.36	1.13	0.87	0.58	0.36		
8.0	2.08	1.46	1.24	1.00	0.73	0.45	0.25		
9.0	2.06	1.38	1.14	0.90	0.63	0.33			
10.0	2.05	1.31	1.07	0.81	0.53	0.26			
12.0	2.03	1.19	0.90	0.65	0.59	0.15			
14.0	2.02	1.07	0.78	0.52	0.28	0.10			
16.0	2.02	0.95	0.67	0.40	0.18	0.06			

TABLE B

C

V/RT	$10^{-36}n^2/IV$								
	0	1	2	4	8	16	32	64	128
0.0	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99	0.99
0.5	1.06	1.06	1.06	1.06	1.06	1.06	1.06	1.05	1.04
1.0	1.22	1.22	1.21	1.21	1.21	1.20	1.19	1.17	1.14
2.0	1.69	1.68	1.68	1.67	1.65	1.61	1.54	1.43	1.22
3.0	2.10	2.08	2.07	2.05	2.01	1.91	1.73	1.47	
4.0	2.29	2.27	2.25	2.21	2.13	1.98	1.73	1.34	
5.0	2.33	2.30	2.27	2.23	2.12	1.89	1.56		
6.0	2.32	2.26	2.22	2.16	2.01	1.70	1.31		
7.0	2.27	2.19	2.12	2.05	1.85	1.52	1.09		
8.0	2.22	2.11	2.04	1.92	1.68	1.34	0.91		
9.0	2.18	2.05	1.94	1.80	1.53	1.19			
10.0	2.15	1.99	1.86	1.68	1.39	1.03			
12.0	2.11	1.89	1.73	1.45	1.15	0.77			
14.0	2.08	1.81	1.61	1.24	0.93	0.55			
16.0	2.06	1.75	1.51	1.06	0.72	0.34			

[*] Pitzer, *J. Chem. Phys.*, **5**, 469 (1937).

TABLE C

$S_f - S_{rr}$

V/RT	$10^{-36}n^2/IV$								
	0	1	2	4	8	16	32	64	128
0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.5	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
1.0	0.12	0.12	0.12	0.12	0.12	0.11	0.11	0.10	0.09
2.0	0.42	0.41	0.41	0.41	0.40	0.38	0.36	0.29	0.21
3.0	0.79	0.77	0.76	0.75	0.74	0.68	0.62	0.47	
4.0	1.13	1.11	1.10	1.08	1.05	0.97	0.84	0.61	
5.0	1.42	1.39	1.37	1.35	1.29	1.18	0.98		
6.0	1.66	1.62	1.60	1.57	1.49	1.34	1.08		
7.0	1.87	1.82	1.79	1.74	1.63	1.44	1.12		
8.0	2.04	1.98	1.95	1.88	1.74	1.50	1.12		
9.0	2.19	2.11	2.07	1.98	1.81	1.54			
10.0	2.32	2.21	2.16	2.06	1.86	1.55			
12.0	2.53	2.37	2.37	2.17	1.91	1.53			
14.0	2.69	2.51	2.42	2.23	1.91	1.46			
16.0	2.83	2.63	2.50	2.27	1.89	1.36			

TABLE D

$(F_{rr} - F_f)/T$

V/RT	$10^{-36}n^2/IV$								
	0	1	2	4	8	16	32	64	128
0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.5	0.47	0.40	0.38	0.36	0.32	0.29	0.23	0.16	0.08
1.0	0.87	0.77	0.73	0.68	0.61	0.53	0.42	0.28	0.12
2.0	1.52	1.35	1.28	1.18	1.04	0.86	0.63	0.35	0.11
3.0	1.98	1.73	1.63	1.49	1.29	1.03	0.70	0.32	
4.0	2.33	1.99	1.85	1.67	1.43	1.10	0.70	0.26	
5.0	2.60	2.18	2.00	1.78	1.50	1.11	0.65		
6.0	2.81	2.30	2.10	1.85	1.52	1.08	0.58		
7.0	2.98	2.39	2.16	1.88	1.51	1.03	0.49		
8.0	3.13	2.45	2.20	1.89	1.48	0.96			
9.0	3.26	2.50	2.22	1.89	1.45	0.88			
10.0	3.38	2.53	2.24	1.88	1.40	0.82			
12.0	3.57	2.57	2.23	1.83	1.31	0.69			
14.0	3.72	2.59	2.21	1.76	1.20	0.57			
16.0	3.86	2.59	2.18	1.68	1.08	0.43			

APPENDIX III

THERMODYNAMIC CONTRIBUTIONS FROM THE HINDERED ROTATION OF A SYMMETRIC TOP

BY BRYCE L. CRAWFORD, JR.

DIRECTIONS FOR USE OF TABLES

The tables are based on the treatment given by Crawford.[1] They consist of the six functions G_V, G_R, H_V, H_R, J_V, and J_R, and of the "zero-point" levels a_0. The first six functions involve two parameters and are given in double-entry tables.

The tables are to be used in the following way: First the contribution due to overall rotation is computed in the usual manner, using the moments of inertia of the molecule as a whole, I_1, I_2, I_3, and a symmetry number obtained by considering the internal rotations to be frozen. To find the contribution of an internal top, of moment of inertia D, whose direction cosines to the principal axes of the molecule are λ_1, λ_2, λ_3, the parameter

$$\Omega = 1 - \sum_i (D/I_i)\lambda_i^2$$

is first calculated. The parameters for the double-entry tables are next found: they are

$$\theta = (8\pi^2 D\Omega/h^2 n^2) V,$$
$$T_V' = (640\pi^2 D\Omega/h^2 n^2) RT,$$
$$T_R' = (640\pi^2 D/h^2 n^2) RT.$$

In these expressions V is the barrier-height and n the number of minima in the potential, assumed to be of the form $(V/2)(1 - \cos n\phi)$, ϕ being the angle of rotation. R is the gas constant, T the absolute temperature, and h is Planck's constant.

The "zero-point" level a_0 is a function of θ alone (Table I). The functions G_V, H_V, J_V are determined from the θ and T_V' (Tables 2A, 3A, 4A), and the functions G_R, H_R, J_R (Tables 2B, 3B, 4B) from θ and T_R'. These functions are combined to give the following:

$$G = (\Omega^{1/2}G_R + G_V); \qquad H = (\Omega^{1/2}H_R + H_V); \qquad J = (\Omega^{1/2}J_R + J_V)$$

and the thermodynamic contributions to the entropy, free energy, energy content, and heat capacity of a single rotor calculated from the formulas:

$$S = R[\ln G + (H/G)],$$
$$F/T = -R[\ln G + (20/T_V')a_0],$$
$$E/T = R[(H/G) - (20/T_V')a_0],$$
$$C = R[(J/G) - (H/G)^2].$$

[1] B. L. Crawford, Jr., *J. Chem. Phys.*, **8**, 273 (1940).

(These give the contributions based on the lowest observable state rather than the bottom of the potential energy curve; they go over into the vibrational contributions from the ordinary vibrational partition function $[1 - \exp(-h\nu/kT)]^{-1}$.)

The tables may be in error by one or two units in the last place given; the J functions may have slightly larger errors. For values of θ above 16, the thermodynamic contributions at low temperatures may be obtained by treating the "internal rotation" as a vibration.

Two sets of values are given for certain values of θ. These mark the points where a change is made in the number of "vibrational" levels taken in the V-type functions; both values are given so that interpolation in θ is facilitated.

It should be remembered that the approximation on which the tables are based breaks down if Ω is very different from 1 as is the case for methyl alcohol. In most applications, this will not occur. For a given value of Ω, the magnitude of the possible error may be estimated from the difference between calculations with, e.g., $\theta = 5$ and $\theta = 5'$ (different number of levels in the V-functions). For molecules in which two identical symmetrical tops rotate about an axis joining them, e.g., ethane, the tables of Appendix II give the correct thermodynamic functions as can be seen by considering the derivations in Section 54.

TABLE 1

θ	a_0	θ	a_0
0	-0.0000	12	-17.3321
1	-0.4551	14	-20.7760
2	-1.5140	16	-24.2587
3	-2.8344	18	-27.7728
4	-4.2805	20	-31.3134
5	-5.8000	24	-38.4590
6	-7.3688	28	-45.6734
7	-8.9737	32	-52.9422
8	-10.6067	36	-60.2556
9	-12.2624	40	-67.6062
10	-13.9370		

TABLE 2A

G_V

T/θ	1'	2	3	4	5	5'	6	7	8	9	10	10'	12	16	16'	θ/T
80	1.120	1.460	2.031	2.916	4.263	4.855	7.024	10.304	15.280	22.853	34.412	34.557	79.482	441.03	441.04	80
100	1.095	1.354	1.763	2.354	3.190	3.847	5.129	6.920	9.423	12.929	17.848	18.022	34.706	134.84	134.88	100
120	1.079	1.287	1.604	2.041	2.629	3.334	4.213	5.379	6.924	8.973	11.691	11.954	20.417	61.859	61.904	120
140	1.067	1.241	1.499	1.843	2.290	3.031	3.690	4.532	5.608	6.979	8.728	9.065	14.191	36.070	36.168	140
160	1.059	1.208	1.425	1.708	2.065	2.834	3.357	3.986	4.816	5.817	7.057	7.448	10.930	24.409	24.547	160
180	1.052	1.183	1.370	1.609	1.905	2.697	3.128	3.654	4.294	5.069	6.000	6.440	8.994	18.202	18.368	180
200	1.046	1.164	1.328	1.534	1.786	2.597	2.963	3.403	3.928	4.554	5.299	5.761	7.740	14.501	14.687	200
220	1.042	1.148	1.294	1.476	1.694	2.520	2.838	3.215	3.659	4.180	4.792	5.288	6.883	12.082	12.299	220
240	1.039	1.134	1.266	1.429	1.622	2.461	2.741	3.070	3.453	3.898	4.414	4.940	6.266	10.421	10.668	240
260	1.036	1.123	1.244	1.390	1.562	2.413	2.664	2.955	3.292	3.678	4.122	4.675	5.803	9.227	9.502	260
280	1.033	1.114	1.224	1.358	1.513	2.374	2.601	2.861	3.162	3.503	3.892	4.468	5.446	8.336	8.636	280
300	1.031	1.106	1.208	1.330	1.472	2.341	2.548	2.784	3.054	3.360	3.704	4.302	5.163	7.650	7.975	300
350	1.026	1.090	1.176	1.277	1.393	2.280	2.449	2.640	2.856	3.096	3.363	4.007	4.665	6.483	6.866	350
400	1.023	1.079	1.152	1.239	1.336	2.237	2.380	2.540	2.719	2.917	3.134	3.814	4.344	5.762	6.193	400
450	1.020	1.070	1.134	1.210	1.294	2.205	2.329	2.469	2.620	2.787	2.970	3.679	4.122	5.277	5.751	450
500	1.018	1.062	1.120	1.187	1.261	2.180	2.290	2.411	2.544	2.689	2.846	3.581	3.960	4.931	5.442	500
600	1.015	1.052	1.099	1.153	1.213	2.146	2.234	2.332	2.437	2.551	2.674	3.447	3.741	4.474	5.045	600
700	1.013	1.044	1.084	1.130	1.180	2.122	2.196	2.278	2.365	2.459	2.560	3.362	3.602	4.188	4.806	700
800	1.011	1.039	1.074	1.113	1.156	2.106	2.169	2.239	2.313	2.393	2.478	3.303	3.505	3.993	4.649	800
900	1.010	1.034	1.065	1.100	1.138	2.093	2.148	2.209	2.274	2.344	2.417	3.260	3.435	3.852	4.540	900
1000	1.009	1.031	1.058	1.089	1.123	2.082	2.132	2.186	2.241	2.306	2.370	3.227	3.381	3.746	4.460	1000

TABLE 2B

G_R

θ/T \ T	0	1	1'	2	3	4	5	5'	6	7	8	9	10	10'	12	16	16'	θ \ T
80	1.773	1.868	.7473	.7093	.6955	.7167	.7706	.1850	.1668	.1568	.1534	.1558	.1635	.01825	.01625	.01651	.001593	80
100	1.982	2.052	.9565	.9161	.8962	.9066	.9524	.2953	.2720	.2580	.2520	.2529	.2604	.04673	.04192	.04079	.006193	100
120	2.170	2.224	1.146	1.105	1.081	1.084	1.118	.4136	.3865	.3690	.3601	.3589	.3648	.08873	.08024	.07626	.01569	120
140	2.346	2.389	1.322	1.281	1.255	1.252	1.277	.5362	.5061	.4859	.4741	.4705	.4714	.1422	.1297	.1217	.03114	140
160	2.510	2.546	1.486	1.446	1.418	1.412	1.430	.6597	.6275	.6049	.5907	.5848	.5864	.2048	.1881	.1753	.05285	160
180	2.662	2.692	1.640	1.601	1.572	1.563	1.575	.7818	.7482	.7237	.7074	.6992	.6987	.2739	.2533	.2352	.08058	180
200	2.802	2.829	1.782	1.745	1.716	1.704	1.712	.9009	.8664	.8404	.8223	.8122	.8096	.3474	.3232	.2998	.1138	200
220	2.935	2.957	1.917	1.881	1.852	1.838	1.842	1.017	.9820	.9547	.9354	.9235	.9190	.4240	.3968	.3651	.1517	220
240	3.068	3.088	2.050	2.016	1.987	1.971	1.973	1.134	1.098	1.070	1.050	1.036	1.030	.5045	.4743	.4405	.1944	240
260	3.197	3.215	2.179	2.145	2.116	2.100	2.099	1.248	1.212	1.184	1.162	1.147	1.139	.5868	.5539	.5154	.2410	260
280	3.319	3.335	2.301	2.268	2.240	2.223	2.220	1.359	1.323	1.294	1.272	1.256	1.247	.6699	.6346	.5918	.2907	280
300	3.435	3.449	2.418	2.386	2.359	2.341	2.337	1.467	1.431	1.402	1.379	1.362	1.351	.7532	.7139	.6691	.3430	300
350	3.706	3.718	2.692	2.662	2.636	2.618	2.610	1.724	1.689	1.659	1.635	1.617	1.604	.9607	.9197	.8645	.4822	350
400	3.959	3.969	2.946	2.920	2.894	2.876	2.867	1.967	1.934	1.904	1.880	1.860	1.845	1.166	1.123	1.061	.6302	400
450	4.200	4.208	3.188	3.163	3.139	3.121	3.110	2.200	2.168	2.138	2.114	2.094	2.078	1.369	1.324	1.257	.7840	450
500	4.431	4.438	3.420	3.396	3.373	3.356	3.344	2.425	2.393	2.364	2.340	2.319	2.303	1.568	1.522	1.452	.9414	500
600	4.866	4.872	3.854	3.834	3.813	3.795	3.783	2.849	2.819	2.792	2.768	2.747	2.730	1.954	1.908	1.832	1.260	600
700	5.266	5.270	4.254	4.235	4.216	4.199	4.187	3.242	3.214	3.188	3.165	3.144	3.127	2.321	2.276	2.196	1.575	700
800	5.631	5.634	4.619	4.603	4.585	4.569	4.557	3.605	3.579	3.551	3.532	3.515	3.494	2.666	2.621	2.541	1.881	800
900	5.964	5.966	4.954	4.938	4.922	4.907	4.896	3.939	3.914	3.891	3.870	3.851	3.834	2.989	2.945	2.864	2.174	900
1000	6.267	6.269	5.260	5.245	5.230	5.216	5.205	4.246	4.223	4.202	4.182	4.163	4.146	3.289	3.247	3.166	2.452	1000

TABLE 3.4

$-H_T$

θ/T	1'	2	3	4	5	5'	6	7	8	9	10	10'	12	16	16'	θ/T
80	.1275	.5526	1.439	3.120	6.182	5.871	11.384	21.032	37.702	66.223	114.66	111.38	333.32	2633.8	2633.8	80
100	.09970	.4099	.9993	2.015	3.700	3.424	6.228	10.707	17.781	28.847	46.029	45.699	112.95	632.54	632.42	100
120	.08191	.3251	.7584	1.458	2.544	2.297	4.018	6.601	10.435	16.076	24.317	23.971	53.238	236.38	236.28	120
140	.06934	.2683	.6066	1.126	1.896	1.674	2.855	4.548	6.949	10.327	15.048	14.678	30.306	114.60	114.36	140
160	.06008	.2281	.5037	.9116	1.493	1.292	2.166	3.375	5.031	7.283	10.324	9.949	19.497	65.714	65.412	160
180	.05306	.1986	.4305	.7588	1.225	1.040	1.723	2.642	3.866	5.485	7.613	7.244	13.658	42.275	41.957	180
200	.04763	.1762	.3763	.6568	1.036	.8657	1.422	2.152	3.104	4.335	5.918	5.563	10.182	29.533	29.220	200
220	.04326	.1584	.3348	.5761	.8962	.7381	1.204	1.805	2.571	3.550	4.781	4.435	7.936	21.795	27.048	220
240	.03944	.1433	.2993	.5102	.7846	.6376	1.035	1.540	2.175	2.969	3.956	3.618	6.363	16.721	16.382	240
260	.03623	.1307	.2709	.4573	.6964	.5591	.9047	1.357	1.874	2.536	3.350	3.021	5.240	13.280	12.922	260
280	.03353	.1203	.2475	.4144	.6259	.4970	.8020	1.179	1.642	2.206	2.892	2.573	4.413	10.853	10.487	280
300	.03123	.1115	.2279	.3791	.5684	.4469	.7195	1.053	1.459	1.948	2.536	2.228	3.786	9.078	8.710	300
350	.02672	.09440	.1906	.3126	.4620	.3555	.5705	.8283	1.135	1.497	1.924	1.640	2.742	6.264	5.897	350
400	.02333	.08183	.1637	.2657	.3884	.2937	.4705	.6791	.9232	1.207	1.537	1.274	2.109	4.658	4.298	400
450	.02068	.07210	.1432	.2305	.3342	.2490	.3986	.5728	.7743	1.006	1.271	1.027	1.691	3.644	3.291	450
500	.01854	.06434	.1270	.2032	.2926	.2154	.3446	.4937	.6643	.8584	1.078	.8516	1.397	2.956	2.613	500
600	.01533	.05282	.1033	.1637	.2334	.1685	.2696	.3846	.5141	.6592	.8210	.6231	1.019	2.103	1.782	600
700	.01306	.04478	.08706	.1370	.1939	.1379	.2208	.3140	.4180	.5330	.6599	.4845	.7926	1.610	1.312	700
800	.01140	.03895	.07537	.1180	.1661	.1168	.1871	.2656	.3523	.4475	.5517	.3940	.6453	1.297	1.021	800
900	.01015	.03458	.06667	.1040	.1457	.1015	.1627	.2306	.3052	.3865	.4749	.3313	.5437	1.084	.8277	900
1000	.009186	.03121	.06000	.09326	.1303	.09001	.1145	.2045	.2701	.3413	.4183	.2860	.4704	.9330	.6928	1000

TABLE 3B

H_R

θ/T	0	1	1'	2	3	4	5	5'	6	7	8	9	10	10'	12	16	16'	θ/T
80	.8863	.7540	.8815	.8664	.8349	.7890	.7261	.4156	.3923	.3759	.3662	.3628	.3651	.04492	.0739	.07341	.01067	80
100	.9909	.8934	.9931	.9869	.9618	.9167	.8529	.5770	.5548	.5360	.5219	.5125	.5076	.1779	.1612	.1505	.03413	100
120	1.085	1.009	1.090	1.091	1.072	1.032	.9717	.7251	.7044	.6861	.6693	.6552	.6442	.2888	.2653	.2440	.07424	120
140	1.173	1.111	1.180	1.185	1.172	1.138	1.082	.8597	.8428	.8245	.8063	.7894	.7737	.4077	.3790	.3472	.1298	140
160	1.255	1.203	1.263	1.272	1.263	1.234	1.184	.9816	.9677	.9510	.9414	.9142	.8953	.5279	.4959	.4549	.1978	160
180	1.331	1.287	1.340	1.351	1.346	1.322	1.277	1.092	1.081	1.066	1.048	1.030	1.009	.6457	.6119	.5638	.2750	180
200	1.401	1.364	1.411	1.424	1.422	1.402	1.362	1.191	1.183	1.171	1.154	1.136	1.114	.7589	.7246	.6714	.3585	200
220	1.467	1.434	1.477	1.491	1.492	1.475	1.440	1.282	1.277	1.266	1.252	1.234	1.213	.8662	.8328	.7763	.4452	220
240	1.534	1.505	1.544	1.559	1.562	1.548	1.517	1.370	1.367	1.358	1.345	1.328	1.308	.9705	.9381	.8795	.5345	240
260	1.598	1.572	1.608	1.624	1.628	1.617	1.589	1.452	1.451	1.444	1.433	1.417	1.398	1.070	1.039	.9794	.6245	260
280	1.659	1.636	1.670	1.685	1.690	1.682	1.658	1.528	1.529	1.524	1.514	1.500	1.482	1.164	1.134	1.075	.7139	280
300	1.717	1.696	1.728	1.743	1.750	1.743	1.722	1.600	1.602	1.599	1.591	1.578	1.561	1.253	1.225	1.168	.8020	300
350	1.853	1.836	1.863	1.879	1.887	1.884	1.869	1.763	1.768	1.768	1.764	1.754	1.739	1.456	1.434	1.382	1.014	350
400	1.980	1.966	1.989	2.005	2.014	2.014	2.003	1.909	1.917	1.919	1.918	1.910	1.899	1.637	1.620	1.576	1.213	400
450	2.100	2.088	2.109	2.124	2.135	2.137	2.129	2.044	2.054	2.058	2.059	2.054	2.045	1.802	1.791	1.753	1.399	450
500	2.216	2.205	2.224	2.239	2.250	2.253	2.248	2.171	2.182	2.188	2.190	2.187	2.181	1.955	1.948	1.916	1.573	500
600	2.433	2.425	2.441	2.455	2.467	2.471	2.469	2.404	2.417	2.425	2.430	2.430	2.428	2.228	2.229	2.206	1.886	600
700	2.633	2.626	2.640	2.653	2.665	2.670	2.670	2.614	2.627	2.637	2.644	2.647	2.647	2.469	2.475	2.458	2.159	700
800	2.816	2.810	2.821	2.834	2.845	2.852	2.853	2.803	2.817	2.827	2.836	2.840	2.842	2.682	2.692	2.677	2.400	800
900	2.982	2.977	2.987	2.998	3.009	3.016	3.019	2.974	2.988	2.999	3.008	3.014	3.018	2.872	2.884	2.870	2.612	900
1000	3.133	3.129	3.138	3.148	3.158	3.166	3.169	3.129	3.142	3.154	3.164	3.170	3.175	3.043	3.057	3.041	2.801	1000

TABLE 4.1

J_V

θ/T	1'	2	3	4	5	5'	6	7	8	9	10	10'	12	16	16'
80	.01451	.2092	1.363	3.339	8.963	9.126	21.497	47.458	99.700	201.73	396.38	396.92	1434.7	15886.0	15886.0
100	.009076	.1241	.5664	1.725	4.292	4.408	9.538	19.397	37.545	69.970	126.53	127.04	387.37	3035.0	3035.4
120	.006220	.08211	.3534	1.0410	2.449	2.548	5.202	10.009	18.347	32.371	55.403	55.848	151.89	939.9	940.2
140	.004505	.05799	.2471	.6884	1.570	1.637	3.202	5.920	10.437	17.712	29.151	29.558	73.996	387.49	388.07
160	.003410	.04307	.1813	.4867	1.080	1.133	2.145	3.849	6.590	10.864	17.366	17.727	41.663	193.01	193.64
180	.002677	.03333	.1373	.3625	.7849	.8303	1.532	2.685	4.494	7.243	11.320	11.636	26.027	109.82	110.41
200	.002168	.02667	.1067	.2814	.6008	.6365	1.150	1.978	3.251	5.146	7.899	8.175	17.506	68.909	69.435
220	.001796	.02158	.08646	.2250	.4741	.5044	.8948	1.517	2.456	3.831	5.794	6.040	12.551	46.211	46.716
240	.001498	.01810	.07081	.1822	.3796	.4054	.7088	1.186	1.896	2.922	4.367	4.585	9.261	32.336	32.819
260	.001267	.01521	.05902	.1504	.3104	.3326	.5744	.9503	1.504	2.293	3.392	3.587	7.071	23.601	24.060
280	.001088	.01299	.05002	.1265	.2589	.2782	.4752	.7788	1.221	1.846	2.707	2.882	5.563	17.862	18.295
300	.0009462	.01124	.04301	.1080	.2195	.2364	.4002	.6504	1.012	1.518	2.209	2.367	4.486	13.925	14.335
350	.0006951	.008173	.03089	.07653	.1532	.1660	.2757	.4407	.5362	.9974	1.430	1.555	2.838	8.232	8.586
400	.0005320	.006208	.02324	.05099	.1129	.1228	.2011	.3174	.4805	.7020	.9951	1.097	1.944	5.357	5.664
450	.0004190	.004860	.01806	.04393	.08630	.09426	.1526	.2384	.3576	.5190	.7279	.8116	1.406	3.722	3.987
500	.0003375	.003897	.01440	.03479	.06788	.07436	.1193	.1549	.2754	.3960	.5527	.6227	1.059	2.713	2.944
600	.0002313	.002652	.009710	.02324	.04490	.04942	.07819	.1195	.1764	.2511	.3468	.3974	.6509	1.602	1.780
700	.0001684	.001920	.006985	.01661	.03185	.03518	.05311	.05371	.1223	.1728	.2369	.2753	.4457	1.049	1.190
800	.0001285	.001461	.005287	.01251	.02386	.02643	.04109	.06201	.09009	.1265	.1726	.2027	.3231	.7402	.8543
900	.0001020	.001156	.004168	.009927	.01866	.02072	.03202	.04808	.06033	.09679	.1320	.1565	.2461	.5528	.6478
1000	.00008359	.0009451	.003397	.007984	.01511	.01680	.02585	.03865	.05570	.07762	.1051	.1255	.1936	.4314	.5122

TABLE 4B

J_R

θ/T	16'	16	12	10'	10	9	8	7	6	5'	5	4	3	2	1'	1	0
80	.0726	.3364	.3627	.4021	.9128	.9690	.9976	1.027	1.057	1.081	1.214	1.332	1.383	1.391	1.361	1.376	1.329
100	.1931	.5846	.6439	.6986	1.208	1.247	1.284	1.316	1.340	1.355	1.471	1.526	1.552	1.543	1.511	1.520	1.486
120	.3640	.8402	.9261	1.014	1.443	1.486	1.522	1.551	1.567	1.572	1.658	1.690	1.699	1.681	1.648	1.654	1.627
140	.5659	1.088	1.190	1.249	1.652	1.692	1.725	1.747	1.756	1.752	1.818	1.834	1.832	1.810	1.777	1.782	1.759
160	.7776	1.322	1.430	1.482	1.837	1.872	1.899	1.914	1.917	1.906	1.958	1.964	1.954	1.929	1.898	1.902	1.882
180	.9963	1.540	1.646	1.688	2.000	2.029	2.050	2.059	2.055	2.040	2.082	2.081	2.065	2.040	2.011	2.014	1.997
200	1.215	1.741	1.838	1.871	2.146	2.167	2.182	2.185	2.175	2.157	2.193	2.186	2.167	2.141	2.116	2.118	2.103
220	1.415	1.921	2.012	2.031	2.274	2.288	2.298	2.296	2.284	2.262	2.292	2.281	2.264	2.237	2.213	2.215	2.201
240	1.608	2.091	2.167	2.181	2.398	2.408	2.412	2.406	2.391	2.367	2.392	2.378	2.360	2.335	2.312	2.314	2.301
260	1.790	2.249	2.307	2.318	2.512	2.519	2.518	2.508	2.491	2.466	2.488	2.472	2.452	2.429	2.407	2.409	2.398
280	1.958	2.392	2.434	2.442	2.617	2.620	2.616	2.604	2.584	2.559	2.578	2.561	2.540	2.518	2.498	2.500	2.489
300	2.114	2.524	2.551	2.555	2.714	2.714	2.707	2.692	2.672	2.647	2.664	2.646	2.623	2.602	2.584	2.585	2.576
350	2.459	2.812	2.809	2.804	2.930	2.922	2.913	2.895	2.873	2.848	2.861	2.842	2.819	2.803	2.786	2.787	2.780
400	2.752	3.057	3.036	3.021	3.123	3.107	3.100	3.080	3.058	3.033	3.043	3.024	3.004	2.989	2.974	2.975	2.969
450	3.010	3.274	3.243	3.218	3.302	3.280	3.274	3.254	3.233	3.209	3.217	3.198	3.181	3.167	3.154	3.154	3.150
500	3.240	3.471	3.434	3.401	3.471	3.445	3.441	3.421	3.401	3.378	3.384	3.366	3.352	3.338	3.326	3.326	3.323
600	3.642	3.822	3.778	3.734	3.786	3.756	3.753	3.733	3.717	3.696	3.700	3.683	3.674	3.661	3.650	3.650	3.650
700	3.984	4.128	4.081	4.034	4.073	4.044	4.040	4.023	4.008	3.989	3.992	3.977	3.970	3.958	3.949	3.949	3.949
800	4.282	4.399	4.350	4.304	4.335	4.310	4.303	4.288	4.274	4.258	4.260	4.247	4.240	4.230	4.221	4.221	4.223
900	4.544	4.640	4.589	4.548	4.574	4.554	4.543	4.529	4.517	4.504	4.506	4.493	4.486	4.477	4.470	4.470	4.473
1000	4.776	4.857	4.803	4.770	4.791	4.778	4.762	4.750	4.738	4.729	4.730	4.719	4.710	4.703	4.696	4.697	4.700

APPENDIX IV*

Debye Functions

(IN CAL. PER DEG. PER MOLE BASED ON $R = 1.9857$) †

TABLE A

C_v

θ/T	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	5.957	5.954	5.945	5.930	5.909	5.883	5.851	5.813	5.770	5.722
1	5.669	5.611	5.549	5.482	5.412	5.337	5.259	5.178	5.094	5.007
2	4.918	4.827	4.737	4.638	4.543	4.444	4.345	4.246	4.147	4.047
3	3.947	3.849	3.750	3.653	3.556	3.459	3.364	3.270	3.178	3.086
4	2.996	2.909	2.822	2.737	2.653	2.573	2.497	2.416	2.343	2.270
5	2.197	2.127	2.059	1.992	1.928	1.867	1.806	1.747	1.690	1.634
6	1.582	1.532	1.481	1.433	1.386	1.341	1.297	1.255	1.214	1.175
7	1.137	1.100	1.065	1.031	0.9985	0.9664	0.9354	0.9062	0.8775	0.8495
8	0.8233	0.7977	0.7735	0.7501	0.7266	0.7042	0.6827	0.6619	0.6422	0.6231
9	0.6041	0.5876	0.5695	0.5523	0.5368	0.5213	0.5064	0.4921	0.4780	0.4647
10	0.4518	0.4392	0.4268	0.4153	0.4041	0.3942	0.3827	0.3725	0.3626	0.3532
11	0.3446	0.3351	0.3264	0.3188	0.3100	0.3022	0.2946	0.2873	0.2802	0.2733
12	0.2667	0.2604	0.2540	0.2480	0.2412	0.2366	0.2311	0.2257	0.2205	0.2155
13	0.2109	0.2061	0.2015	0.1969	0.1926	0.1883	0.1842	0.1802	0.1762	0.1725
14	0.1688	0.1652	0.1619	0.1585	0.1552	0.1520	0.1489	0.1458	0.1430	0.1401
15	0.1373	0.1346	0.1320	0.1295	0.1270	0.1246	0.1222	0.1199	0.1177	0.1155

TABLE B

$$\frac{E - E_0}{T}$$

θ/T	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	5.957	5.7354	5.5221	5.3131	5.1110	4.9141	4.7234	4.5381	4.3590	4.1854
1	4.0175	3.8551	3.6983	3.5465	3.4002	3.2590	3.1229	2.9920	2.8660	2.7446
2	2.6280	2.5159	2.4090	2.3046	2.2054	2.1097	2.0182	1.9327	1.8468	1.7662
3	1.6891	1.6154	1.5450	1.4778	1.4134	1.3516	1.2903	1.2365	1.1830	1.1314
4	1.0824	1.0359	0.9912	0.9486	0.9077	0.8692	0.8330	0.7968	0.7635	0.7317
5	0.7007	0.6714	0.6435	0.6167	0.5914	0.5676	0.5443	0.5222	0.5012	0.4809
6	0.4610	0.4440	0.4266	0.4101	0.3942	0.3790	0.3644	0.3507	0.3374	0.3249
7	0.3129	0.3013	0.2903	0.2798	0.2698	0.2601	0.2508	0.2421	0.2337	0.2255
8	0.2179	0.2105	0.2037	0.1969	0.1900	0.1838	0.1778	0.1720	0.1665	0.1612
9	0.1560	0.1514	0.1465	0.1419	0.1376	0.1335	0.1295	0.1257	0.1219	0.1184
10	0.1149	0.1116	0.1083	0.1052	0.1024	0.09984	0.09685	0.9420	0.09164	0.08920
11	0.08697	0.08453	0.08228	0.08032	0.07808	0.07607	0.07415	0.07226	0.07045	0.06869
12	0.0672	0.0656	0.0641	0.0626	0.0611	0.0595	0.0580	0.0565	0.0552	0.0540
13	0.0526	0.0514	0.0502	0.0491	0.0481	0.0471	0.0461	0.0451	0.0441	0.0431
14	0.0420	0.0411	0.0403	0.0395	0.0388	0.0380	0.0373	0.0365	0.0358	0.0350
15	0.0343	0.0335	0.0328	0.0320	0.0313	0.0308	0.0303	0.0298	0.0293	0.0288

TABLE C

$$\frac{E_0 - F}{T}$$

θ/T	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	∞	15.925	12.014	9.815	8.314	7.195	6.316	5.601	5.009	4.505
1	4.079	3.696	3.366	3.077	2.820	2.591	2.385	2.199	2.032	1.879
2	1.7422	1.6168	1.5025	1.3975	1.3017	1.2134	1.1325	1.0587	0.9893	0.9259
3	0.8673	0.8132	0.7629	0.7165	0.6733	0.6332	0.5952	0.5613	0.5291	0.4990
4	0.4709	0.4449	0.4204	0.3976	0.3762	0.3563	0.3379	0.3200	0.3037	0.2884
5	0.2739	0.2602	0.2475	0.2353	0.2241	0.2136	0.2030	0.1940	0.1851	0.1776
6	0.1685	0.1614	0.1543	0.1477	0.1413	0.1353	0.1295	0.1242	0.1191	0.1143
7	0.1097	0.1054	0.1012	0.09730	0.09357	0.09002	0.08660	0.08342	0.08033	0.07737
8	0.07464	0.07199	0.06951	0.06706	0.06467	0.06247	0.06035	0.05831	0.05640	0.05455
9	0.05273	0.05114	0.04944	0.04783	0.04638	0.04494	0.04357	0.04226	0.04098	0.03977
10	0.03859	0.03746	0.03635	0.03527	0.03432	0.03344	0.03243	0.03153	0.03066	0.02984
11	0.02909	0.02826	0.02751	0.02685	0.02609	0.02541	0.02477	0.02414	0.02353	0.02294
12	0.0224	0.0218	0.0213	0.0208	0.0203	0.0198	0.0193	0.0188	0.0184	0.0180
13	0.0175	0.0172	0.0167	0.0164	0.0160	0.0157	0.0154	0.0150	0.0147	0.0144
14	0.0140	0.0137	0.0134	0.0132	0.0129	0.0126	0.0124	0.0122	0.0119	0.0117

* Taken from Landolt-Börnstein, Physikalisch-Chemische Tabellen, Vol. I, 1927.

† To convert to the units adopted in this Treatise ($R = 1.9869$) multiply by 1.00060.

APPENDIX

TABLE A

Basic Constants

Atomic weights, chemical scale (O = 16.0000)
$$^1H = 1.007856 \pm 0.000018$$
$$^2H = 2.014182 \pm 0.000021$$

Velocity of light, $c = (2.99776 \pm 0.00004) \times 10^{10}$ cm. sec.$^{-1}$

Molar volume (0° C., 1 atm.), $V_n = 22414.6 \pm 0.6$ cm.^{3} mole^{-1}

Normal atmosphere, $A_n = 1.013249 \times 10^6$ dyne cm.$^{-2}$

Mechanical equivalent, $J_{15} = 4.1855$ abs. joule cal$_{15}$.$^{-1}$

Faraday (chemical scale), $F = 96501 \pm 10$ int. coul. g.-equiv.$^{-1}$
$$= 96487 \pm 10 \text{ abs. coul. g.-equiv.}^{-1}$$
$$= 9648.7 \pm 1 \text{ abs. e.m.u. g.-equiv.}^{-1}$$
$$Fc = 2.89247 \times 10^{14} \text{ abs. e.s.u. g.-equiv.}^{-1}$$

Electronic charge, $e = (4.8025 \pm 0.001) \times 10^{-10}$ abs. e.s.u.

Specific electronic charge, $e/m_0 = (1.7592 \pm 0.0005) \times 10^7$ abs. e.m.u. g.$^{-1}$
$$c(e/m_0) = (5.2736 \pm 0.0015) \times 10^{17} \text{ abs. e.s.u. g.}^{-1}$$

Rydberg constant for infinite mass, $R_\infty = 109{,}737.30 \pm 0.05$ cm.$^{-1}$

Ratio of grating to Siegbahn system of X-ray wave lengths, $\lambda_g/\lambda_s = 1.002034 \pm 0.00006$

True grating space of calcite (20° C.), $d_{20} = 3.03567 \pm 0.00018$Å

1 international amp. = 0.99986 abs. amp.

1 international volt = 1.00034 abs. volt

TABLE B

Derived Constants

1 abs. volt electron, $10F/J_{15} = 23{,}055$ cal. mole^{-1}

Molar gas constant, $R = V_n A_n/273.15$
$$= 8.31436 \times 10^7 \text{ erg deg.}^{-1} \text{ mole}^{-1}$$
$$10^{-7}R/J_{15} = 1.9869 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$
$$1.9869/\log_{10} e = 4.575$$

Avogadro number, $N = Fc/e = 6.0227 \times 10^{23}$ mole^{-1}

Boltzmann constant, $k = R/N = 1.38047 \times 10^{-16}$ erg deg.$^{-1}$

Kinetic energy per mole at $T_0 = 273.15$, $E_0 = \frac{3}{2}T_0$
$$= 5.656 \times 10^{-14} \text{ erg}$$

Energy of 1 abs. volt electron, $10^8 e/c = 1.60203 \times 10^{-12}$ erg

Energy in electron volts correspond to $E_0 = 3.531 \times 10^{-2}$ abs. volt

Mass of electron, $m_0 = ec^{-1}(e/m_0)^{-1} = 9.1066 \times 10^{-28}$ g.

Mass of atom ^1H, $m_H = 1.007857/N_0 = 1.67339 \times 10^{-24}$ g.

Mass of proton, $m_p = m_H - m_0 = 1.67248 \times 10^{-24}$ g.

Ratio, $m_p/m_0 = 1837.6$

Speed of V abs. volt electron, $v = \{2 \times 10^8(e/m_0)V\}^{1/2}$
$$= 5.9314 \times 10^7 \sqrt{V} \text{ cm. sec.}^{-1}$$

Temperature associated with 1 abs. volt electron, $10^8 e/ck = 11{,}604$ deg. K. abs. volt^{-1}

Planck's constant, $h = \left\{ \frac{2\pi^2}{c^2} \cdot \frac{e^5}{R_\infty} \cdot \left(\frac{m_0}{e} \right) \right\}^{1/3}$
$$= (6.6242 \pm 0.0024) \times 10^{-27} \text{ erg sec.}$$

Bohr unit of angular momentum, $h/2\pi = 1.0542 \times 10^{-27}$ erg sec.

Potential associated with unit frequency, $V/\nu = h/e = 1.3793 \times 10^{-17}$ erg sec. e.s.u. $^{-1}$

Abs. volts associated with unit frequency, $V/\nu = (h/e)c \times 10^{-8} = 4.1349 \times 10^{-15}$ abs. volt sec.

Frequency associated with unit abs. volt,
$$\nu/V = (e/h)(10^8/c) = 2.4185 \times 10^{14} \text{ sec.}^{-1} \text{ abs. volt}^{-1}$$

Frequency associated with unit abs. volt, $\nu/V = (e/h)(10^8/c) = 2.4185 \times 10^{14}$ sec.$^{-1}$ abs. volt^{-1}

Energy associated with unit wave number, $E/\bar{\nu} = hc = 1.9856 \times 10^{-16}$ erg cm.

Wave number associated with 1 abs. volt, $\bar{\nu}_0 = 10^8 c^{-2} h/e = 8067.5$ cm.$^{-1}$ abs. volt^{-1}

Energy associated with R_∞, $= 1.9856 \times 10^{-16} R_\infty = 2.179 \times 10^{-11}$ erg
$$= R_\infty/\bar{\nu}_0 = 13.60 \text{ abs. e.v.}$$

Wave length associated with 1 abs. volt, $\lambda_0 = 1/\bar{\nu}_0 = 12395.4 \times 10^{-8}$ cm. abs. volt^{-1}

Radius of normal Bohr orbit, $a_0 = h^2/4\pi^2 m_0 e^2 = 0.5292 \times 10^{-8}$ cm.

Magnetic moment of Bohr magneton, $\mu_B = (h/4\pi)(e/m_0) = 9.273 \times 10^{-21}$ erg gauss^{-1}
$$N\mu_B = 5585.2 \text{ erg gauss}^{-1} \text{ mole}^{-1}$$

Zeeman displacement per gauss, $\Delta\bar{\nu}/H = (e/m_0)/(4\pi c) = 4.6699 \times 10^{-5}$ cm.$^{-1}$ gauss^{-1}

Fine structure constant, $\alpha = 2\pi e^2/hc = 7.297 \times 10^{-3}$
$$\alpha^2 = 5.325 \times 10^{-5}$$

Spectroscopic doublet constant, $R_\infty \alpha^2 = 5.843$ cm.$^{-1}$

Atomic specific heat, $\beta = h/k = 4.7979 \times 10^{-11}$ sec. deg.

Compton shift, $\Delta\lambda = h/m_0 c = 2.4263 \times 10^{-10}$ cm.

Radiation constants:

$$c_1 = 2\pi c^2 h = 3.7400 \times 10^{-5} \text{ erg cm.}^2 \text{ sec.}^{-1}$$
$$c_2 = ch/k = 1.4385 \text{ cm. deg.}$$
$$A = \lambda_m T = 0.28972 \text{ cm. deg.}$$
$$\sigma = \frac{2}{15} \cdot \frac{\pi^5 k^4}{c^2 h^3} = 5.6728 \times 10^{-5} \text{ erg cm.}^{-2} \text{ deg.}^{-4} \text{ sec.}^{-1}$$
$$a = 4\sigma/c = 7.569 \times 10^{-15} \text{ erg cm.}^{-3} \text{ deg.}^{-4}$$

Schroedinger constants:

$$8\pi^2 m_0/h^2 = 1.639 \times 10^{27} \text{ erg}^{-1} \text{ cm.}^{-2}; \ (8\pi^2 m_0 E/h^2 = 4\pi^2/\lambda^2)$$
$$= 2.625 \times 10^{15} \text{ abs. volt}^{-1} \text{ cm.}^{-2}$$
$$h^2/8\pi^2 m_0 = 6.102 \times 10^{-28} \text{ erg cm.}^2$$
$$= 3.809 \times 10^{-16} \text{ abs. volt cm.}^2$$
$$h^2/8m_0 = 6.022 \times 10^{-27} \text{ erg cm.}^2; \ (E_k = (k/L)^2 h^2/8m_0)$$
$$= 3.759 \times 10^{-15} \text{ abs. volt cm.}^2$$
$$2m_0/h^2 = 6.650 \times 10^{13} \text{ abs. volt}^{-1} \text{ cm.}^{-2}; \ (2m_0 E/h^2 = 1/\lambda^2)$$

De Broglie Wave Length, $\lambda = h/mv = h/\sqrt{2m_0 E} = (12.263 \times 10^{-8}/\sqrt{\text{Volts}})$ cm.

INDEX